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- (1) THE ADDITION OF METHYL RADICALS TO VINYL CHLORIDE.
- (2) MASS SPECTROMETRY OF LYCOPODIUM ALKALOIDS.

by

ALAN M. HOGG

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "THE ADDITION OF METHYL RADICALS TO VINYL CHLORIDE. MASS SPECTROMETRY OF LYCOPODIUM ALKALOIDS." submitted by Alan M. Hogg in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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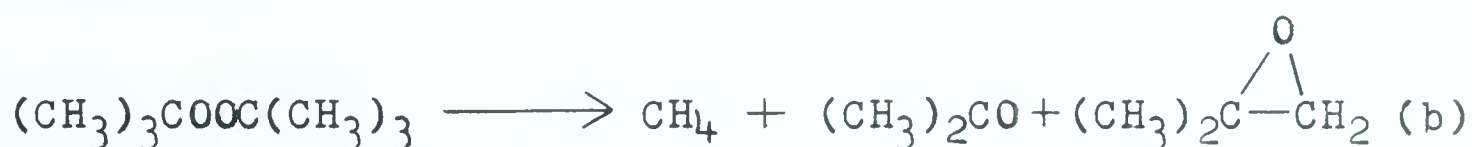
Mrs. G. Conway for the typing of this manuscript.

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ABSTRACTS

(1) Addition of Methyl Radicals to Vinyl Chloride.

The pyrolysis of di-tert.-butyl peroxide (DTBP) has been studied. It was found that the rate of decomposition of the peroxide was increased, and the distribution of decomposition products significantly altered, by the presence of even small amounts of vinyl chloride. In this "catalyzed" decomposition the overall equation (a) which obtains in the normal pyrolysis tends to be replaced by equation (b).



It is shown that this is caused by the formation of chlorine atoms by the reaction of methyl radicals with vinyl chloride. The chlorine atoms abstract hydrogen rapidly from the DTBP to form HCl, and methyl radicals abstract hydrogen from the HCl to form methane. Isobutylene oxide arises from the decomposition of the peroxy radical formed by the hydrogen abstraction from DTBP.

This catalytic effect is found to be common to several other chlorinated compounds.

When the thermal reactor was packed with lime glass Rashig rings, the catalytic effect of the vinyl chloride was completely

suppressed and the addition reaction of methyl radicals to vinyl chloride could be studied. The cause of the suppression appears to be the rapid adsorption of HCl on the glass surface and some adsorption studies were undertaken to gain information about this.

An Arrhenius expression for the rate of addition of methyl radicals to vinyl chloride was obtained and it is

$$k_{\text{addn.}} = 1.3 \times 10^{-11} e^{-9053/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

(2) Mass Spectrometry of Lycopodium Alkaloids.

The mass spectra of a number of lycopodium alkaloids were studied. It was found that the loss of the "bridge" ring together with the hydrogen on C-12 gave rise to the most intense ion in the majority of cases. Further loss of ethylene by a reverse Diels Alder reaction from this ion was also observed.

Alkaloids with hydroxyl groups can be recognized by losses of 17, 18 and 19 mass units and also 18 mass unit "gaps" in the spectrum. -OAc substituted alkaloids were found to give peaks at $m/e=60$ and also at $M-59$ and $M-60$. Methyl esters give peaks at $m/e=59$.

Below $m/e=150$ the spectra showed a "fingerprint" region which was very similar for all lycopodine-type alkaloids but was significantly different for alkaloids with different basic skeletons.

In the light of these "rules" and other observations, the spectra of some uncharacterized alkaloids were examined and in some cases structures could be proposed with reasonable certainty.

An alkaloid isolated from L. Clavatum was shown to be a diol with the probable structure of 11,12-dehydrodesacetyllyco-clavine.

"Alkaloid L-9" was shown to be a molecular complex of lycopodine and O-acetyllofoline.

Sauroxine was shown to be closely related in structure to α -obscurine and is very probably a stereoisomer differing only in the configuration at C-12.

The mass spectrum of lyconnotine was shown to be in complete accord with a recently proposed structure.

Some information was also obtained about the, as yet uncharacterized, alkaloids annopodine, cernuine, lycocernuine and diacetylserratinine.

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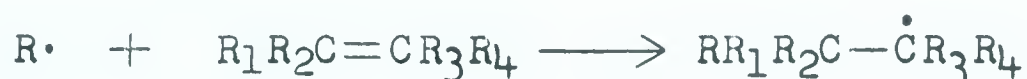
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INTRODUCTION.

Early in the study of the kinetics of reactions in the gas phase it was realized that the overall reactions were the net result of a number of elementary reactions. In postulating possible reaction schemes Rice and Hertzfeld introduced the ideas of free radicals as short lived intermediaries. Their existence has since been conclusively proved and it has been found that free radicals are present in a large proportion of gaseous reactions.

If a full understanding of these reactions is to be arrived at it is necessary to study all the varied types of reactions and an increasing number of chemists are engaged in this pursuit.

Wherever an unsaturated linkage exists in a substrate exposed to radical attack a possible reaction is the addition of a radical $R\cdot$ according to the reaction



In this introduction we will confine ourselves to the discussion of this one type of elementary reaction.

Three factors involved in this reaction may be considered of principal interest to the chemist. These are: the absolute value of the rate constant, the variation of the rate constant with the nature of the substituents $R_1 - R_4$, and finally the variation of the rate constant with the nature of the attacking radical R . For experimental reasons, which we will discuss shortly, it is difficult to obtain accurate Arrhenius expressions for the absolute value of







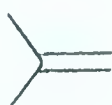
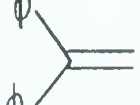
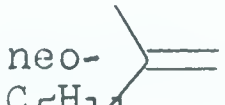
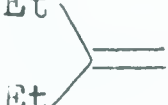
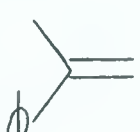
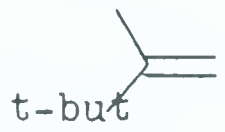





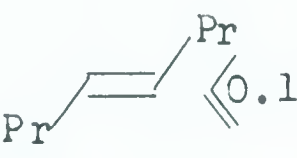
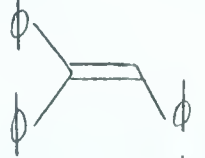

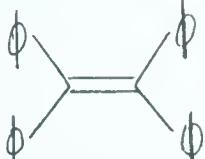
the rate constant. On the otherhand it is comparatively easy to obtain relative rates of addition at one temperature of a radical to various olefins. By this means the effect of the structure of the olefin on the reaction rate can be determined.

The most extensive work of this kind has been done by Szwarc and co-workers (1, 2) in isooctane solution using methyl radicals generated by the thermal decomposition of acetyl peroxide and comparing the rate of addition to the olefin with the rate of hydrogen abstraction from isooctane. If we consider the two series of methyl and phenyl substituted ethylenes and express the rates relative to the monosubstituted compound being unity, we obtain the values shown in Table I (page 3). Thus it appears that alkyl or aryl substitution at one end of the double bond increases reactivity but if both ends are substituted it is decreased. Unfortunately it is not possible with these data to determine whether these effects are exerted through the preexponential factor or the activation energy. Work of James and Steacie (3) in the gas phase seems to parallel this work as also does work of Kharasch and Sage using $\text{CCl}_3\cdot$ radicals (40). These results are also shown in Table I (page 3).

Data on the relative rates of addition of methyl to isolated, conjugated and cumulated dienes have also been obtained by Szwarc over a range of temperatures (5). He shows that isolated dienes behave analogously to olefins while conjugated ones have, as one might expect due to the stable allylic radical formed on addition, a low activation energy for addition. Cumulated dienes were found to be very unreactive and he concluded that this was due to low pre-

TABLE 1

Effect of Substituent Groups on the Reactivity of Double Bonds
Towards Radical Addition.

(a) CH ₃ •	(b) CH ₃ •	(c) C ₂ H ₅ •	(d) CCl ₃ •
 1.6	 0.02		
 1.0	 1.0	 1.0	 1.0
 1.7	 2.0	 2.3	 1.4
	 1.2	 1.1	
 0.12		 <0.2	 0.2
 0.24	 0.13	 <<0.1	
	 0.06		 0.9
	 <0.01		

(a) R. P. Buckley and M. Szwarc. Proc. Roy. Soc. A240, 396 (1957)

(b) F. Leavitt, M. Levy, M. Szwarc. and V. Stannett. J. Am. Chem. Soc. 77, 5493 (1955)

(c) D. G. L. James and E. W. R. Steacie. Proc. Roy. Soc. A244, 297 (1958)

(d) M. S. Kharasch and M. Sage. J. Org. Chem. 14, 537 (1949)

exponential factors. He also found that it was the central C atom in allene to which addition took place.

This work, it must be remembered, was done in solution and while great care was taken to ensure the accuracy of the interpretation of the data one cannot expect it to agree exactly with gas phase work. (Szwarc has found that methyl affinities i.e. the ratio of the rate of addition of methyl to an olefin to the rate of H abstraction from isooctane relative to benzene set equal to 1 are about 10-15% lower when measured in the gas phase (6)).

Work in the gas phase has been directed mainly at finding accurate Arrhenius expressions to describe particular reactions rather than general surveys of relative rates of addition of radicals to various olefins. Such work is of considerable importance and although a fair measure of agreement has been reached between studies carried out under different conditions the experimental difficulties are such that no one investigation can be considered to give unequivocal data. It will be worthwhile, therefore, to discuss in detail some of the techniques used.

The Determination of Rates of Addition of Radicals to Double Bonds.

The experimental difficulties inherent in such investigations have been long recognized and they stem from two basic causes:

- (a) Free radicals have such an ephemeral existence that no simple direct means of measuring their concentration in a system is available.*

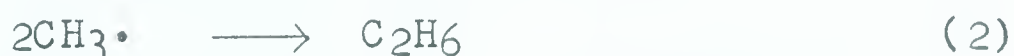
* While physical methods like mass spectrometry, electron spin resonance and U.V. absorption spectroscopy (in flash photolysis) have been of great importance in detection and structural elucidation of free radicals, their use in gas kinetics has hitherto been less successful.

(b) When radicals add to an olefin the product is also a free radical which can frequently undergo a variety of subsequent reactions.

While both of these difficulties can be circumvented, the experimental techniques become indirect and depend on a postulated reaction mechanism which very often has to have simplifying assumptions applied to it so as to make it more tractable. As a result the final conclusions are open to a certain amount of doubt and data obtained are of low precision due to the indirect methods by which they are obtained.

Perhaps these difficulties can best be illustrated with references to specific examples.

If we consider methods of production and measurement of methyl radicals the photolysis of acetone is one possibility. The reaction has been studied extensively (7) within the temperature range 100°C. - 280°C. and can be adequately described by the scheme:



It is found experimentally that:

$$\frac{(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4} + R_{\text{C}_2\text{H}_5\text{COCH}_3})}{R_{\text{CO}}} = 1.90$$

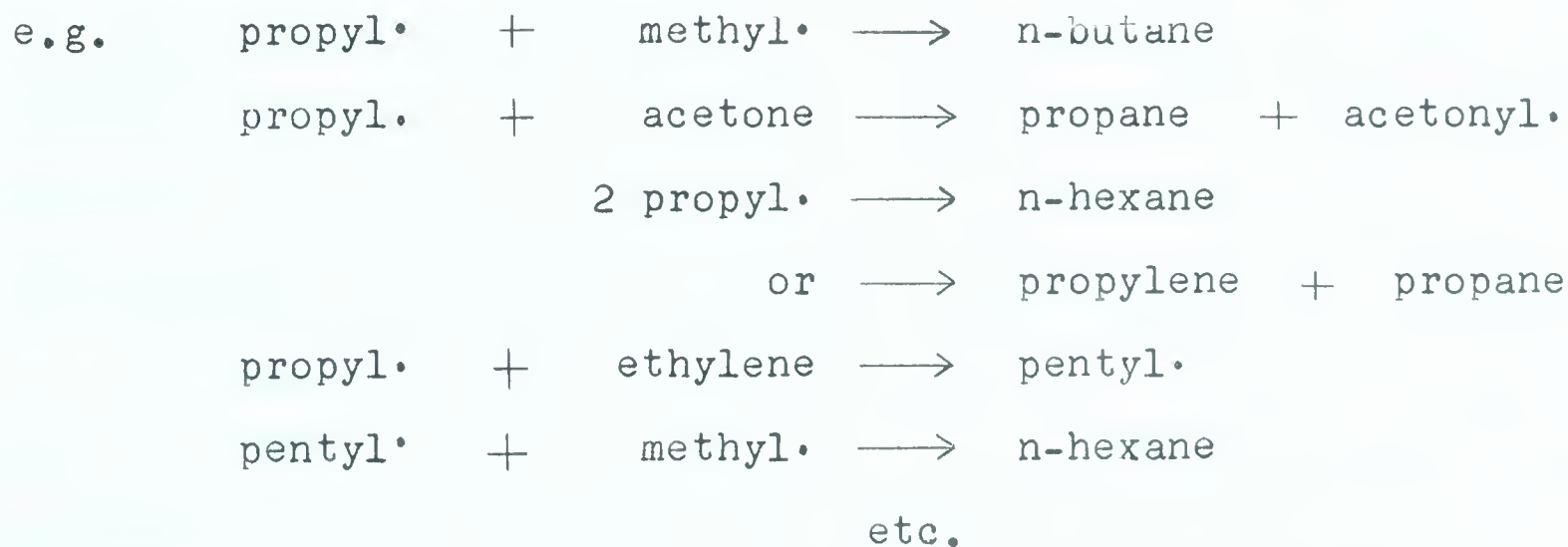
Thus the fate of 95% of the methyl radicals is accounted for by this simple kinetic scheme. If we are to use this reaction as a source of methyl radicals we can use the rate of production of

carbon monoxide as a measure of their rate of production

$$R_{CO} = \frac{1}{2}R_{CH_3}$$

and it only remains for us to measure the rates of formation of all the other products in the reaction system and, by interpretation of these data in the light of an adequate kinetic scheme, we can obtain the reaction parameters we desire. The mass balance between carbon monoxide and the products of the methyl radical reactions will provide a suitable check on the correctness of the interpretation.

Let us assume that ethylene is the olefin which is to be studied. Methyl radicals will be able to react with it to give propyl radicals and the propyl radicals will have a variety of reaction paths open to them.



Thus the analysis system must be capable of detecting and measuring accurately carbon monoxide, methane, ethane, methyl ethyl ketone, propane, propylene, n-butane, n-hexane, etc. in the presence of large amounts of acetone and ethylene. Until the advent of gas chromatography, such a task was almost impossible and even with this valuable tool the errors in measurement tend to be cumulative. It is also found that when the products are many and varied, they must be fractionated and each fraction analyzed

on a suitable column. This procedure usually entails some loss of material and consequent inaccuracy.

If we do not attempt the ideal of collecting and measuring all the products, it is still possible to measure just carbon monoxide, methane, ethane, and methyl ethyl ketone and using the equation

$$\frac{(2R_{C_2H_6} + R_{CH_4} + R_{C_2H_5COCH_3} + R^*)}{R_{CO}} = 1.90$$

determine R^* , the rate of disappearance of methyl radicals.

R^* can be assumed to be equal to the rate of addition only if the propyl radical proceeds on its path towards a stable product without involving another methyl radical.

In several investigations (7, 8) a compromise has been struck between the ideal of total analysis and the mass balance method so that the simplifying assumptions made in the interpretation of the experimental data do not introduce too much error.

Perhaps the earliest successful attempt to collect quantitative data on radical addition reactions was the investigation of the addition of methyl radicals made by Mandelcorn and Steacie in 1954 (8). They used the photolysis of acetone as a source of methyl radicals. They reasoned that if, in the presence of an unsaturated hydrocarbon, the only other reaction of the methyl radicals is addition and R_{CO} is unaffected the rate of addition, R_A' , can be obtained from

$$\frac{(2R_{C_2H_6} + R_{CH_4} + R_{C_2H_5COCH_3} + R_A')}{R_{CO}} = 1.90$$

However methyl radicals may combine with the product of addition



thus making R_A' higher than the true rate of addition.

Since ethane and methane account for most of the methyl radicals produced, it would be expected that the greatest effect of the addition reaction would be on the $(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4})$ portion thus

$$\frac{(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4} + R_A'')}{R_{\text{CO}}}$$

could be equated with

$$\frac{(2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4})}{R_{\text{CO}}}$$

in the absence of the unsaturated hydrocarbon.

R_A'' may be expected to be lower than R_A' particularly at high temperatures.

A further rate of addition, R_A''' , can be obtained by equating the rate of addition with the rate of disappearance of the unsaturated. Some substrate could however be removed by polymerization, hydrogen abstraction or reaction with acetyl radicals.

The similarity between the values of the Arrhenius parameters obtained by all three methods in the ethylene experiments and the latter two in experiments with the other olefins, justify the simplifying assumptions used.

Madelcorn and Steacie reported activation energies for the addition of methyl radicals to ethylene, propylene, acetylene and

butadiene as 7.0, 6.0, 5.5 and about 2.5 kcal./mole respectively.

As is frequently the case in such rate determinations, what was actually measured was $k_{\text{addition}}/(k_{\text{combination of CH}_3})^{\frac{1}{2}}$. However it is now generally assumed (9, 10) that the combination of methyl radicals requires no activation energy and so

$$(E_{\text{addition}} - \frac{1}{2}E_{\text{combination of CH}_3}) \simeq E_{\text{addition}}$$

Since these investigations several others have been made but we will confine ourselves to those which studied the addition of methyl and ethyl radicals to ethylene because these are the ones which will be most directly comparable with the methyl radical/vinyl chloride system.

In 1957 Landers and Volman (11) used the thermal decomposition of di-tert-butyl peroxide, DTBP, to produce methyl radicals which were found to initiate the polymerization of ethylene. They report values of 8.2 and 5.6 kcal./mole for the activation energy for the addition of methyl to ethylene and propylene respectively, but they did not adequately differentiate between this initial addition and subsequent polymerization steps.

Also in 1957 Pinder and Leroy (12) studied the addition of ethyl radicals to ethylene. These authors produced the ethyl radical by the mercury photosensitized decomposition of hydrogen in the presence of ethylene. Their reaction scheme was as follows:



As the ethylene pressure is raised:



If all the butyl radicals formed in (5) disappear by (6)

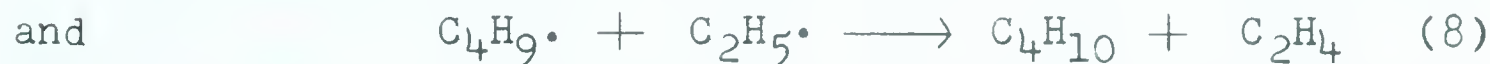
$$R_{\text{C}_6\text{H}_{14}} = k_5(\text{C}_2\text{H}_5\cdot)(\text{C}_2\text{H}_4)$$

If butane is only formed by reaction (3)

$$\frac{R_{\text{C}_6\text{H}_{14}}}{R_{\text{C}_4\text{H}_{10}}^{\frac{1}{2}}} = \frac{k_5}{k_3^{\frac{1}{2}}(\text{C}_2\text{H}_4)}$$

A correction for the distribution of the $\text{C}_2\text{H}_5\cdot$ throughout the reaction vessel was applied and analysis was made by means of gas chromatography.

It was shown that if:



are of importance then the values of $k_5/k_3^{\frac{1}{2}}$ would be strongly dependent on the ethylene pressure and this is not the case.

The results give:

$$E_5 - \frac{1}{2}E_3 = 5.5 \text{ kcal./mole}$$

If we use Shepp and Kutschke's (13) value for E_3 (combination of ethyl radicals) of 2.0 kcal./mole we obtain

$$E_{\text{addition of ethyl to ethylene}} = 6.5 \text{ kcal./mole}$$

In 1958 Brinton (14) reinvestigated the addition of methyl radicals to ethylene using DTBP as a source of methyl radicals but he used low concentrations of ethylene and prevented the polymerization which was present in the similar investigation by Landers and Volman. Brinton found that the rate constant of

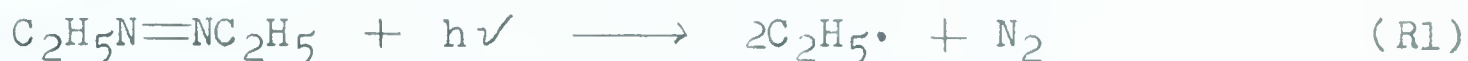
addition relative to the square root of the rate constant for combination of methyl radicals.

$$\frac{k_{4a}}{k_3^{\frac{1}{2}}} = 3.3 \times 10^{-7} e^{-8860/RT} \text{ cc}^{\frac{1}{2}} \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$$

(Reaction numerals are from original paper.)

In 1959 Lampe and Field (15) used the photolysis of azoethane to determine the addition of ethyl radicals to ethylene.

Their reaction scheme was as follows:



If ethylene is added to the system, some of the ethyl radicals formed in (R1) will add to it to form butyl radicals i.e.



The absence of significant amounts of octane in the products leads them to assume, as an approximation, that butyl radicals react only with ethyl radicals, as might be expected if the concentration of the ethyl radicals was sufficiently high.



The usual steady state approximation leads to

$$\left(\frac{1}{(\text{C}_2\text{H}_4)} \right) \left(\frac{R_{\text{C}_6\text{H}_{14}}}{R_{\text{C}_4\text{H}_{10}}^{\frac{1}{2}}} \right) = P_c \left(\frac{k_4}{k_3^{\frac{1}{2}}} \right)$$

where P_c is the probability that in (R5) - (R7) coupling occurs.

i.e.

$$P_c = \frac{k_5}{(k_5 + k_6 + k_7)}$$

Their results indicated that P_c was very close to unity so as an approximation (considered by them to be not in error by more than 5 or 10%) they set $P_c = 1$ and derived an Arrhenius plot from runs at three different temperatures. This gave:

$$\frac{k_4}{k_3^{1/2}} = 2.6 \times 10^{-9} e^{-5500/RT} \text{ cc}^{1/2} \text{ molecule}^{-1/2} \text{ sec}^{-1/2}$$

If we allow 1 kcal./mole for $\frac{1}{2}E_3$ we get

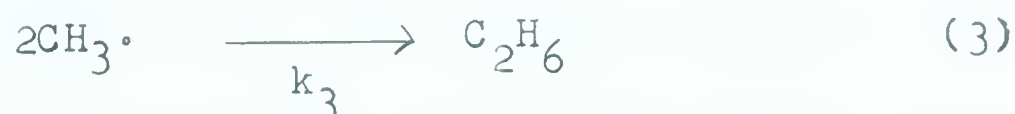
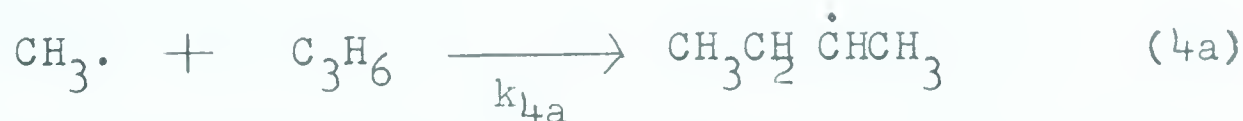
$$E_{\text{addition}} = 6.5 \text{ kcal./mole}$$

which is in very good agreement with Pinder and Leroy's work.

Recently (1962) Miyoshi and Brinton (16) have applied the same experimental technique to the study of the methyl radical/propylene reaction as Brinton used in his ethylene experiments. Gas chromatography was used in this case to analyze for the larger variety of products and their results give:

$$\frac{k_{4a}}{k_3^{1/2}} = 2.07 \times 10^{-7} e^{-8800/RT} \text{ cc}^{1/2} \text{ molecule}^{-1/2} \text{ sec}^{-1/2}$$

where



While the investigations quoted above and summarised in Table II (page 13) are the only ones involving the addition of small radicals to small olefins and as such have a direct bearing on the work to be reported here, several larger radicals have been added to olefins larger than propylene. The results of these investigations are well

TABLE II

Literature Values for Rates of Addition of Small
Radicals to Small Olefins in the Gas Phase.

Radical	Substrate	log k 140°C (a)	log A (a)	E (b)	Reference
CH ₃	CH ₂ =CH ₂	4.6	9.2	8.9	Brinton (1958) (14)
CH ₃	CH ₂ =CH ₂	4.7	8.6	7.0	Mandelcorn & Steacie (1954) (8)
CH ₃	CH ₂ =CH ₂	4.5	8.7	7.8	This Study
C ₂ H ₅	CH ₂ =CH ₂	4.4	7.3	6.5	Lampe & Field (1959) (15)
C ₂ H ₅	CH ₂ =CH ₂	4.1	7.0	6.5	Pinder & Leroy (1957) (12)
CH ₃	CH ₂ =CHCH ₃	4.7	9.0	8.8	Miyoshi & Brinton (1962) (16)
CH ₃	CH ₂ =CHCH ₃	5.2	8.6	6.0	Mandelcorn & Steacie (1954) (8)
CH ₃	CH ₂ =CHCl	5.1	9.9	9.1	This Study

(a) mole l.⁻¹sec.⁻¹

(b) kcal. mole⁻¹

summarised by Trotman-Dickenson (17).

The main feature of these other results is the constancy of the activation energies which lie mostly in the range 6-8 kcal./mole.

Purpose of This Study and Choice of Experimental Technique.

Szwarc and coworkers (5) have carried out a very extensive study of methyl radical addition to double bonds in solution. This work has included an investigation of the effect of heteroatoms on the addition reaction. They showed that the presence of a chlorine atom in the α position (but not in the terminal position) to the double bond increases the rate of methyl radical addition very considerably. For example, the rate of methyl radical addition at 65°C to chloroprene is three times faster than that to butadiene and isoprene. Also in unpublished work he has found that methyl adds to vinyl chloride about 28 times faster than to ethylene (6).

He has shown that fluorine also has an activating effect on the addition of radicals to double bonds and suggests that any electron withdrawing group will have a similar effect. Conversely electron donating groups will have a deactivating effect. He advances the following explanation (18).

As the radical approaches the double bond of an olefin its uncoupled p electron cloud will be repelled by the π electron cloud of the olefin. At closer proximity one of the π electrons will become localized and, as its orbital overlaps the p orbital of the radical, exchange will lead to an attraction and finally the bond will be formed. This can be illustrated by a section of the

potential energy surface as shown in Fig. 1a (page 16).

The actual reaction path is shown by the heavy line and the difference between the point where the attractive and repulsive curves cross and the line representing the unexcited states of the olefin and radical at infinite separation will be the activation energy.

If the olefin has an electron withdrawing substituent, the π charge cloud will be reduced and so there will be less repulsion as the p orbital of the radical approaches it. This can be shown on the potential energy diagram Fig. 1b (page 16) by a flatter repulsive curve. It will be seen that the activation energy for the reaction is thus reduced.

No work has so far been reported on additions of radicals to hetero atom substituted olefins in the gas phase and the present investigation was undertaken in order to obtain such data and by comparison with the results obtained with the corresponding unsubstituted olefins, to determine in particular whether the activating effect of chlorine substitution could be observed in the gas phase. The methyl radical/vinyl chloride system is the simplest structurally and was the one chosen for this investigation.

Published quantitative studies on vinyl chloride are limited to investigations of its polymerization (19, 20). In particular Burnett and Wright (20) have studied the polymerization in tetrahydrofuran solvent. Under irradiation with a mercury arc with a small amount of 2,2-azo-isobutyronitrile or 1,1-azo-1-cyclohexane as initiator, the vinyl chloride was found to polymerize. By using intermittent illumination by means of a rotating sector and

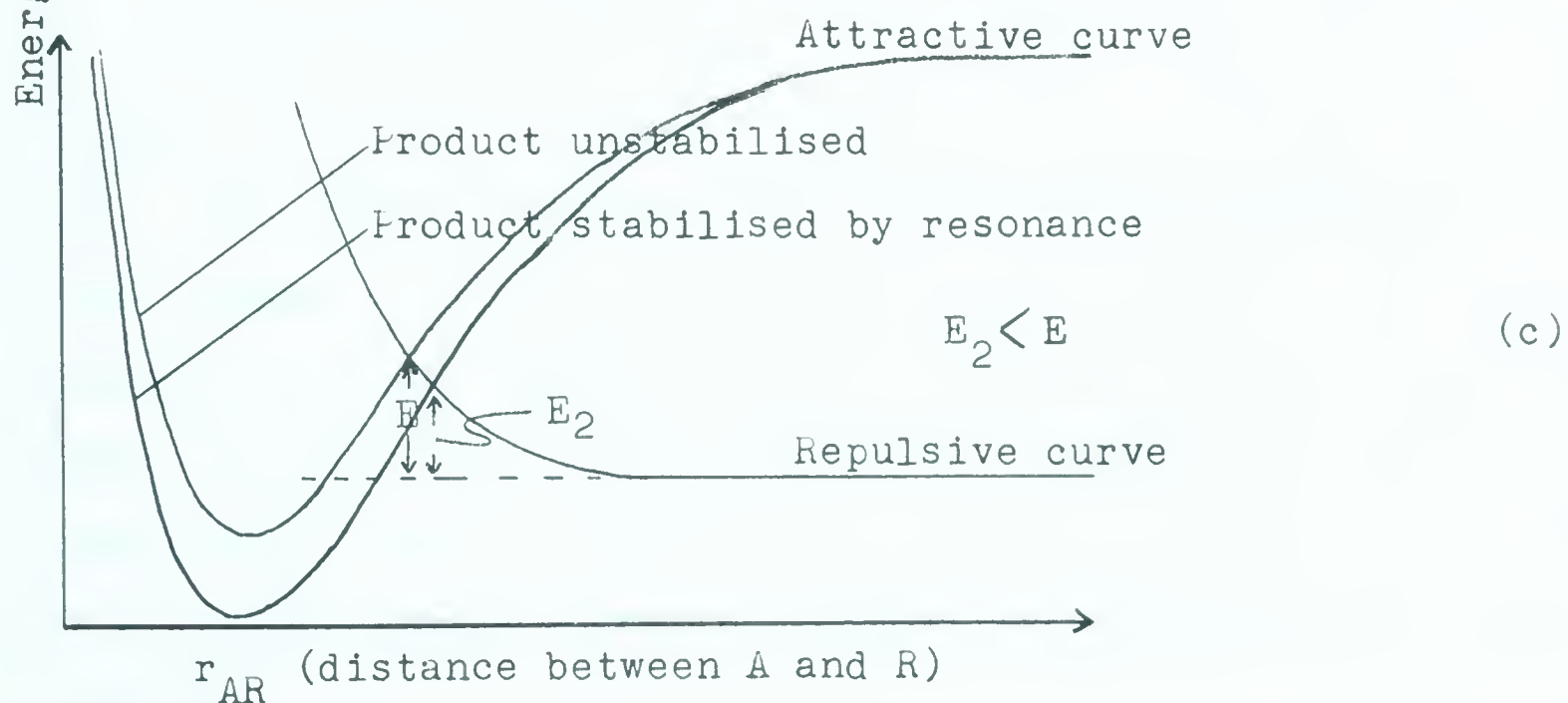
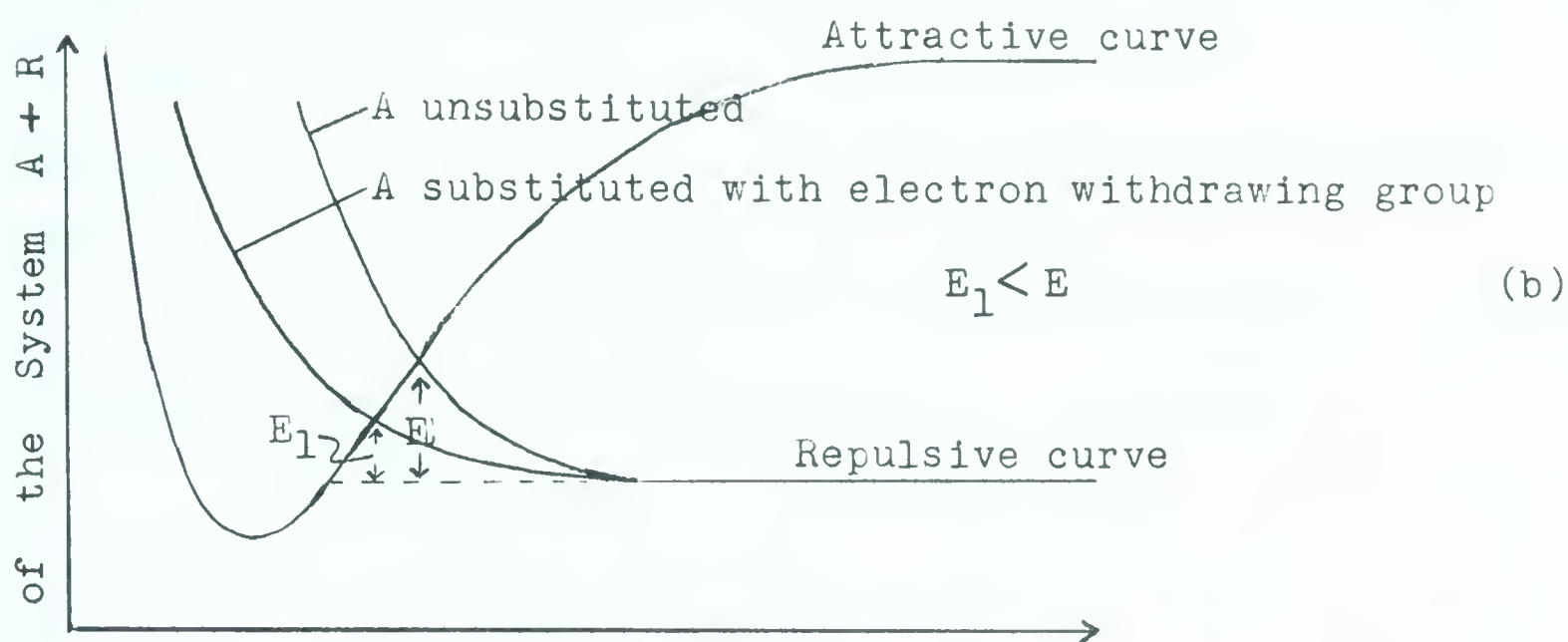
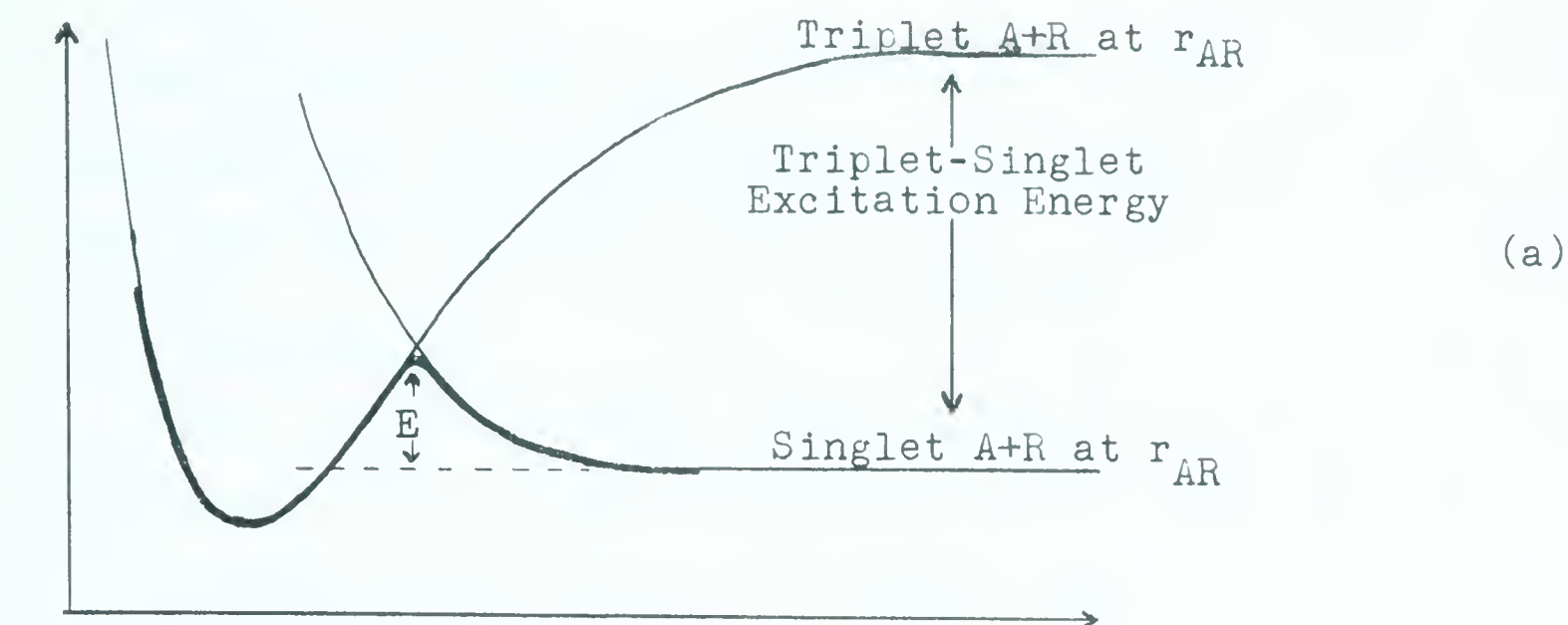


Fig. 1 Hypothetical potential energy surface cross sections for radical addition reactions.

a theory which is developed in a previous publication (21) they determined the rate of propagation at two different temperatures (25°C and 55°C) and obtained the Arrhenius expression

$$k_{\text{propagation}} = 5.5 \times 10^{-15} e^{-3700/RT} \text{ cc molecule}^{-1} \text{ sec}^{-1}$$

This value, of course, refers to an average rate constant of addition over all stages of the polymerization chain.

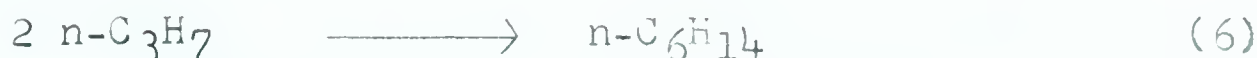
Of the possible sources of methyl radicals available for this study, the one adopted by Brinton (14, 16) in his work with ethylene and propylene, namely the thermal decomposition of DTBP, seemed particularly attractive and this was the one used. We will therefore discuss these results in more detail.

It has been shown (22, 23, 24) that in the temperature range 120-160°C DTBP decomposes according to the scheme:

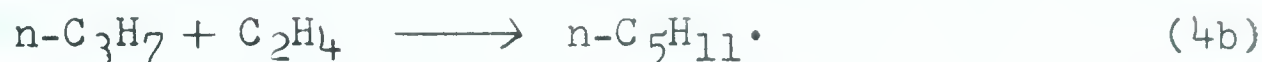


In his study of the reaction of methyl radicals with ethylene Brinton found that hydrogen abstraction from ethylene was unimportant. The addition reaction led to n-butane predominately although some propane, propylene and n-hexane were produced. The apparent absence of higher molecular weight material led him to conclude that the polymerization of ethylene is prevented by the relatively large methyl radical concentration and the reaction can be explained by a kinetic scheme which in addition to reactions (1) - (3) above requires:





While it might be expected that the hexane originates also from the reactions:



Brinton shows that this is not the case by the following rationale.

(a) If all the hexane is formed by propyl radical combination (6) then:

$$R_{\text{C}_6\text{H}_{14}} = k_6(\text{C}_3\text{H}_7)^{\frac{1}{2}} \quad \text{and} \quad R_{\text{C}_2\text{H}_6} = k_3(\text{CH}_3)^2$$

$$R_{\text{C}_4\text{H}_{10}} = k_5(\text{CH}_3)(\text{C}_3\text{H}_7\cdot)$$

$$\frac{R_{\text{C}_4\text{H}_{10}}}{R_{\text{C}_6\text{H}_{14}}^{\frac{1}{2}} \cdot R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}} = \frac{k_5}{k_6^{\frac{1}{2}} k_3^{\frac{1}{2}}}$$

(b) If all the hexane is formed by propyl addition to ethylene (4b) and subsequent combination with a methyl radical (7).

$$R_{\text{C}_6\text{H}_{14}} = k_7(\text{CH}_3)(\text{C}_5\text{H}_{11}) = k_6(\text{C}_3\text{H}_7)(\text{C}_2\text{H}_4)$$

$$R_{\text{C}_2\text{H}_6} = k_3(\text{CH}_3)^2$$

$$R_{\text{C}_4\text{H}_{10}} = k_5(\text{CH}_3)(\text{C}_3\text{H}_7)$$

$$\frac{R_{\text{C}_4\text{H}_{10}}(\text{C}_2\text{H}_4)}{R_{\text{C}_6\text{H}_{14}} \cdot R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}} = \frac{k_5}{k_4 k_3^{\frac{1}{2}}}$$

He calculates the two quantities

$$\frac{R_{C_4H_{10}}}{R_{C_6H_{14}}^{\frac{1}{2}} \cdot R_{C_2H_6}^{\frac{1}{2}}} \quad \text{and} \quad \frac{R_{C_4H_{10}}(C_2H_4)}{R_{C_6H_{14}} \cdot R_{C_2H_6}^{\frac{1}{2}}}$$

and shows that while the former is a constant at about 1.4 independent of both ethylene concentration and temperature, the latter is not constant varying with both ethylene concentration and temperature.

The rate of the reaction (4a) is determined by considering a steady state concentration of propyl radicals which gives:

$$\begin{aligned} \frac{d(C_3H_7)}{dt} &= k_{4a}(CH_3)(C_2H_4) - k_5(CH_3)(C_3H_7) - 2(k_6 + k_{6'}) (C_3H_7)^2 = 0 \\ &= k_{4a}(CH_3)(C_2H_4) - R_{C_4H_{10}}(5) - 2R_{C_6H_{14}}(6) - 2R_{C_3H_8}(6) \end{aligned}$$

The ratio of the relative rates of disproportionation to combination of propyl radicals has been determined by Whiteway and Masson (25) to be 0.13 in the photolysis of di-n-propyl ketone. Using this ratio in his kinetic treatment, therefore, Brinton obtains:

$$\frac{k_{4a}(CH_3)(C_2H_4)}{R_{C_2H_6}^{\frac{1}{2}}} = \frac{k_{4a}}{k_3^{\frac{1}{2}}(C_2H_4)} = \frac{(R_{C_4H_{10}} + 2.26R_{C_6H_{14}})}{R_{C_2H_6}^{\frac{1}{2}}}$$

Thus by plotting $(R_{C_4H_{10}} + 2.26R_{C_6H_{14}})R_{C_2H_6}^{\frac{1}{2}}$ versus ethylene concentration a value of $k_{4a}/k_3^{\frac{1}{2}}$ is found from the slope.

He determines such values at three different temperatures and by making an Arrhenius plot of $\log k_{4a}/k_3^{\frac{1}{2}}$ versus $1/T$ he obtains the value:

$$\frac{k_{4a}}{k_3^{\frac{1}{2}}} = 3.3 \times 10^{-7} e^{-8860/RT} \quad \text{cc}^{\frac{1}{2}} \text{molecule}^{-\frac{1}{2}} \text{sec}^{-\frac{1}{2}}$$

EXPERIMENTAL

The apparatus shown in Fig. 2 (page 21) was used throughout the investigation. The procedure adopted in each run was as follows.

A quantity of vinyl chloride was admitted to the evacuated mixing bulb C from the vinyl chloride storage bulb B, the pressure being measured on the mercury manometer M_1 in experiments where relatively high pressures were used, or on the octoil-S manometer M_2 where low pressures were used. The levels of the liquid columns in the manometers were measured by means of a cathetometer. The vinyl chloride was then condensed in the sidearm S by immersing it in liquid nitrogen. With the mixing bulb C isolated from the rest of the system by its stopcock, liquid DTBP was allowed to evaporate into the bulb A until it was filled to a pressure of approximately 10.3 mm measured on the mercury manometer.

Bulbs A and C were now interconnected by manipulation of suitable stopcocks and the DTBP was also condensed in the sidearm S.

The bulb C was again isolated from the system and the condensed mixture in the sidearm was allowed to reevaporate. Mild heating of the glass to about 50°C with an I.R. lamp hastened the reevaporation.

The peroxide/vinyl chloride mixture was now allowed to expand into the reactor by opening the three-way stopcock SC_1 for 10 seconds. After the required reaction time (5 minutes at 158.5°C, 30 minutes at 140°C and 3 hours at 124°C) the stopcock SC_1 was

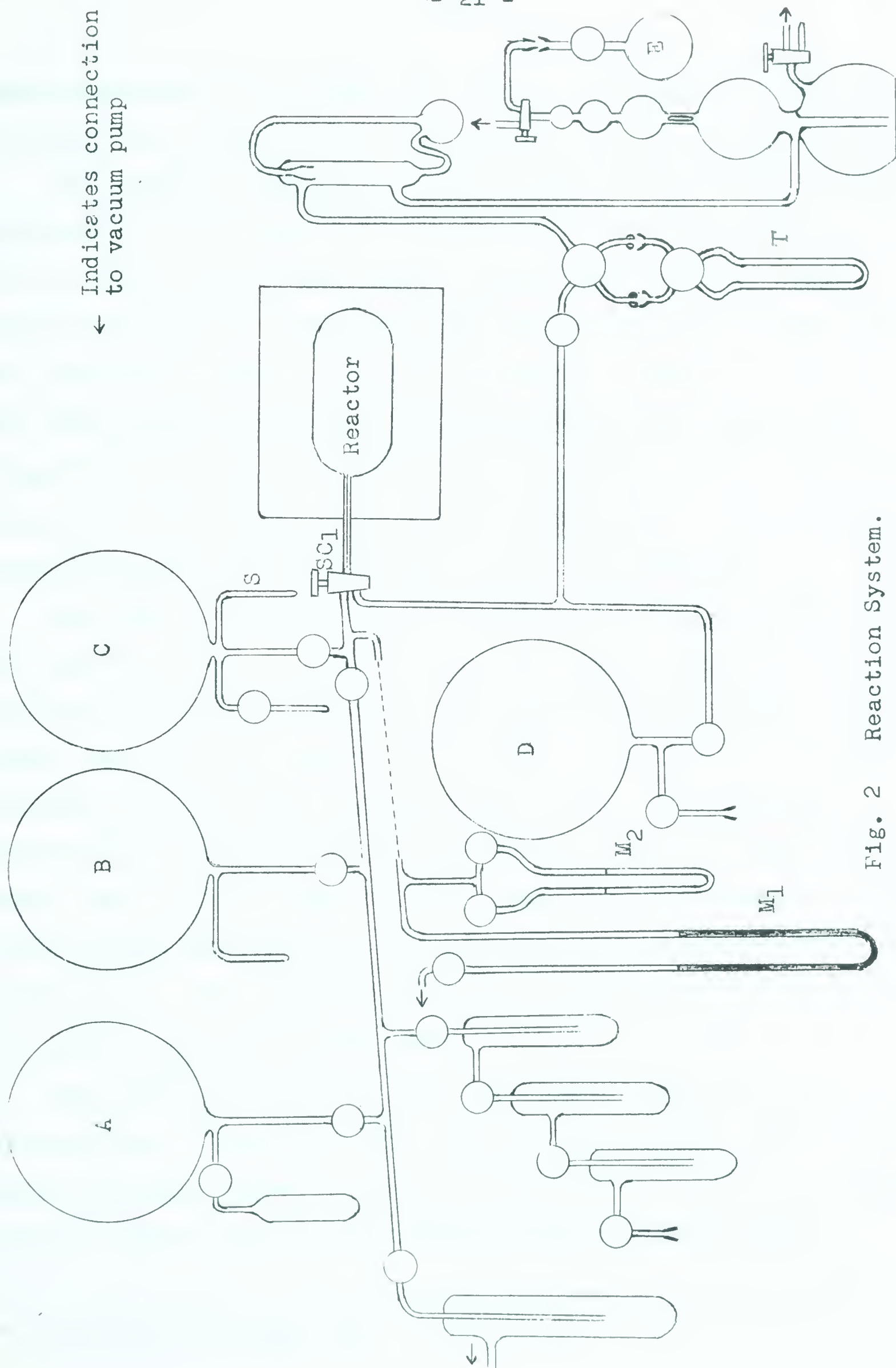


Fig. 2 Reaction System.

again opened for 10 seconds, this time in the opposite direction allowing the reacted mixture to expand into the evacuated bulb D.

The method of analysis of the reacted mixture varied slightly depending on the purpose of a particular experiment. However in most runs the mixture was pumped through the removable trap T which was cooled in liquid nitrogen and the non-condensable portion measured by means of a Toepler pump/gas burette. A sample of the non-condensable portion could be expanded into bulb E and transferred to a mass spectrometer for analysis. The condensable portion of the reacted mixture was transferred to a gas chromatography apparatus in the removable trap T for analysis.

The DTBP used in this investigation was kindly supplied by the Shell Oil Co. of Canada and was purified by repeated trap to trap distillation in vacuo in the reactant inlet system. The middle fraction from these distillations was stored in a sidearm attached to bulb A and isolated from it by a metal stopcock. Occasionally as solid peroxide was melting in one of the traps after the liquid nitrogen had been removed a mild explosion occurred which necessitated repairs to the system and a repetition of the distillation. The purified peroxide gave only one peak on any of the chromatographic columns used.*

The vinyl chloride was also purified by repeated trap to trap distillation in vacuo in the reactant inlet system. Mass spectrometric analysis showed no impurities nor did it give rise to more than one peak on any of the chromatographic columns used.*

* See Table III (page 30)

Thermal Reactors.

During the course of the investigation three reactors were used. These are illustrated in Figs. 3, 4 and 5 (pages 24, 25 and 26).

Unpacked Reactor: This consisted of a cylindrical pyrex vessel of 375 cc. capacity with hemispherical ends. To one end was attached a capillary tube through which reactants could be admitted and removed. An aluminum block consisting of three pieces which bolted together was machined so as to fit around the reactor leaving no more than about 1/10 inch clearance at any point. The cylinder was wrapped with asbestos paper and a nichrome heating element was wound on top of the asbestos and secured at each end by means of a circular copper band. More asbestos paper was wound on top of the heating wires. The heater was found to have an output of 520 watts at 115 v.. The aluminum block was supported on an asbestos cradle mounted on the bottom of an asbestos box. A further asbestos box enclosed the whole assembly, the boxes being attached by asbestos spacers at the bottom and the interspace packed with glass wool. Two glass lined thermocouple wells were drilled in the aluminum block and iron/constantan thermocouples inserted in them.

The unpacked reactor had no thermostat as such but it was found that when the power for the electric heater was supplied by a Powerstat autotransformer, whose primary current was in turn supplied by a 115 v. Sorensen voltage regulator, the temperature varied by less than 0.5 centigrade degrees over 30 minutes reaction

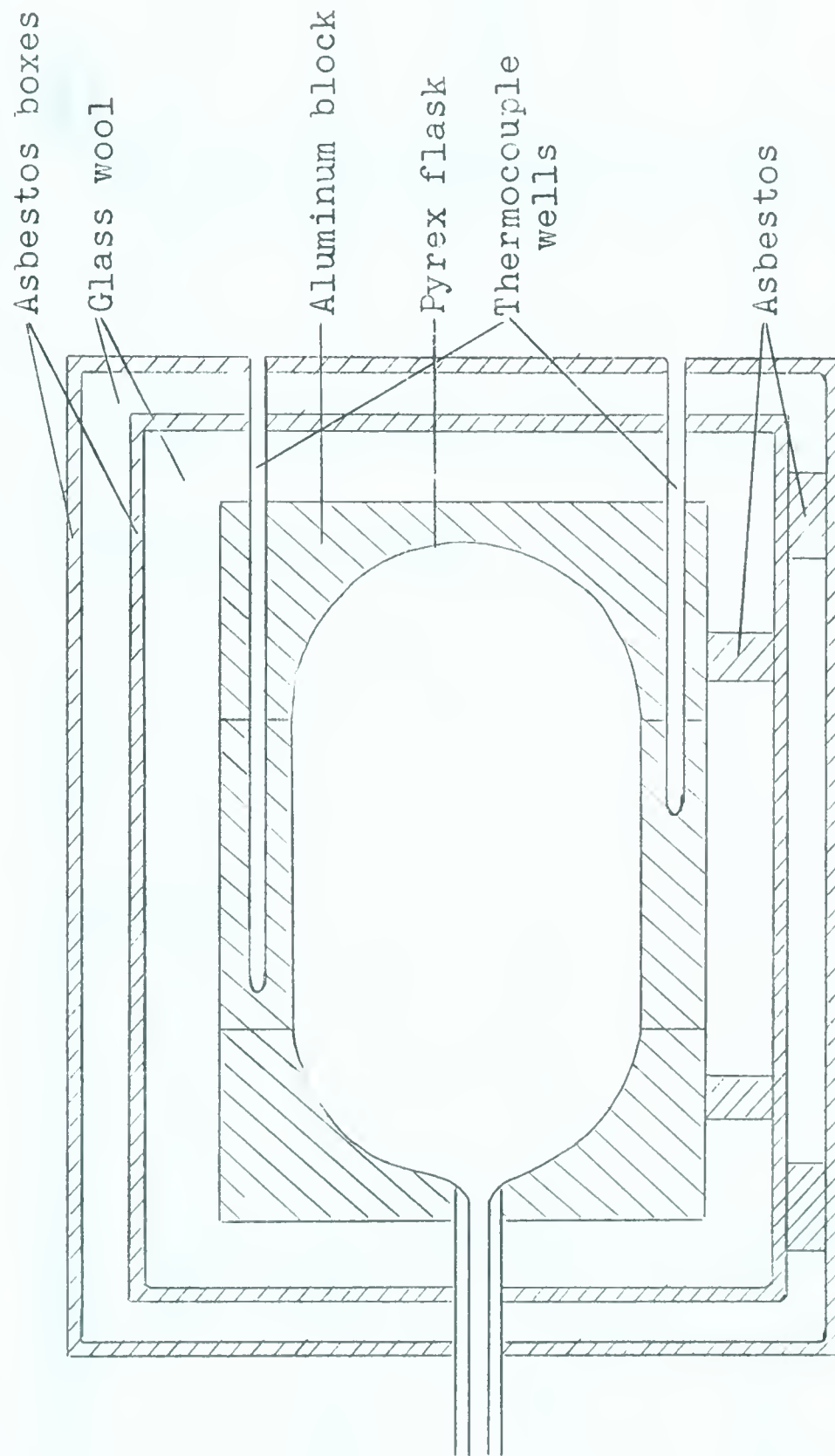


Fig. 3 Unpacked Reactor

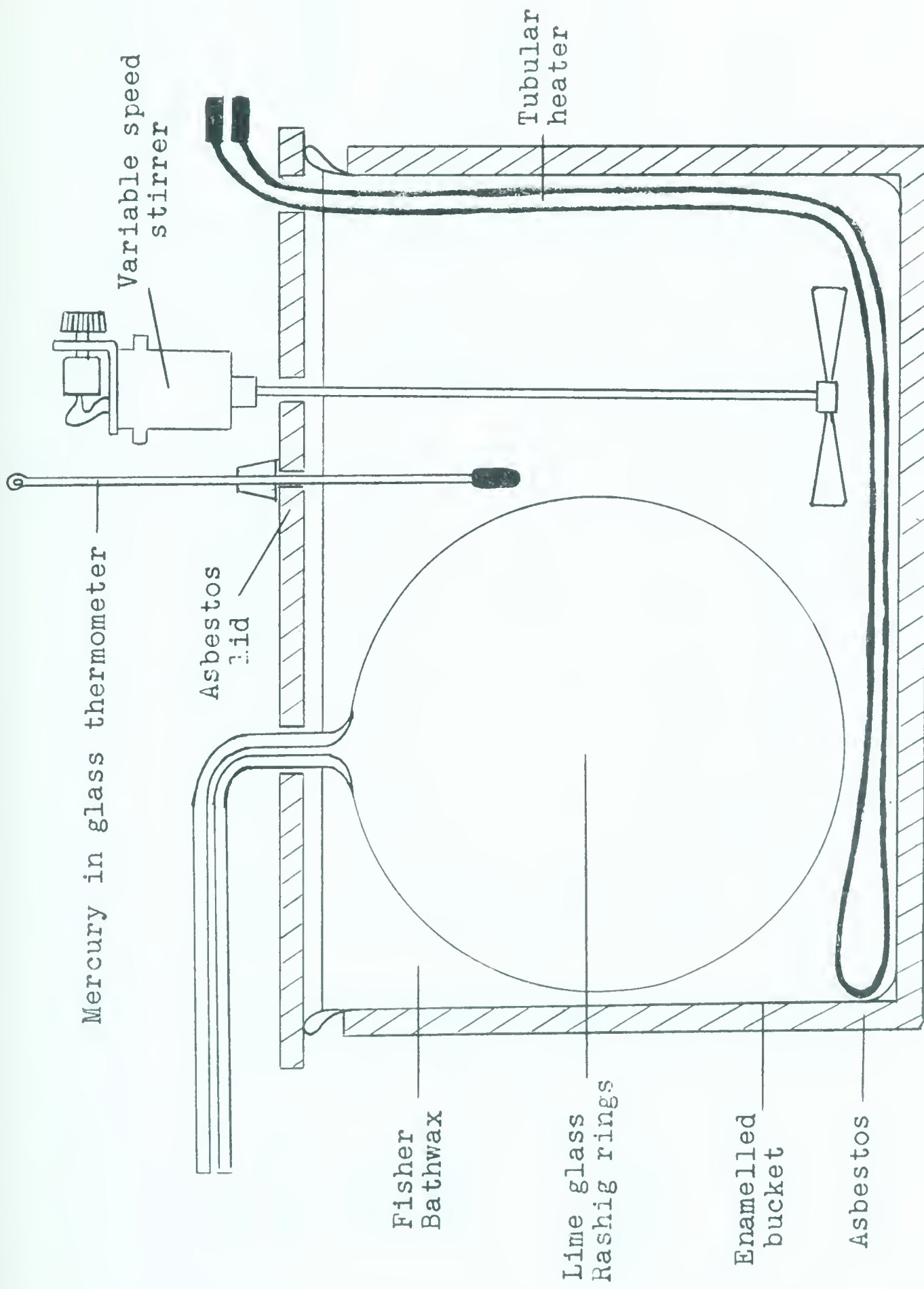


Fig. 4 Packed Reactor #1

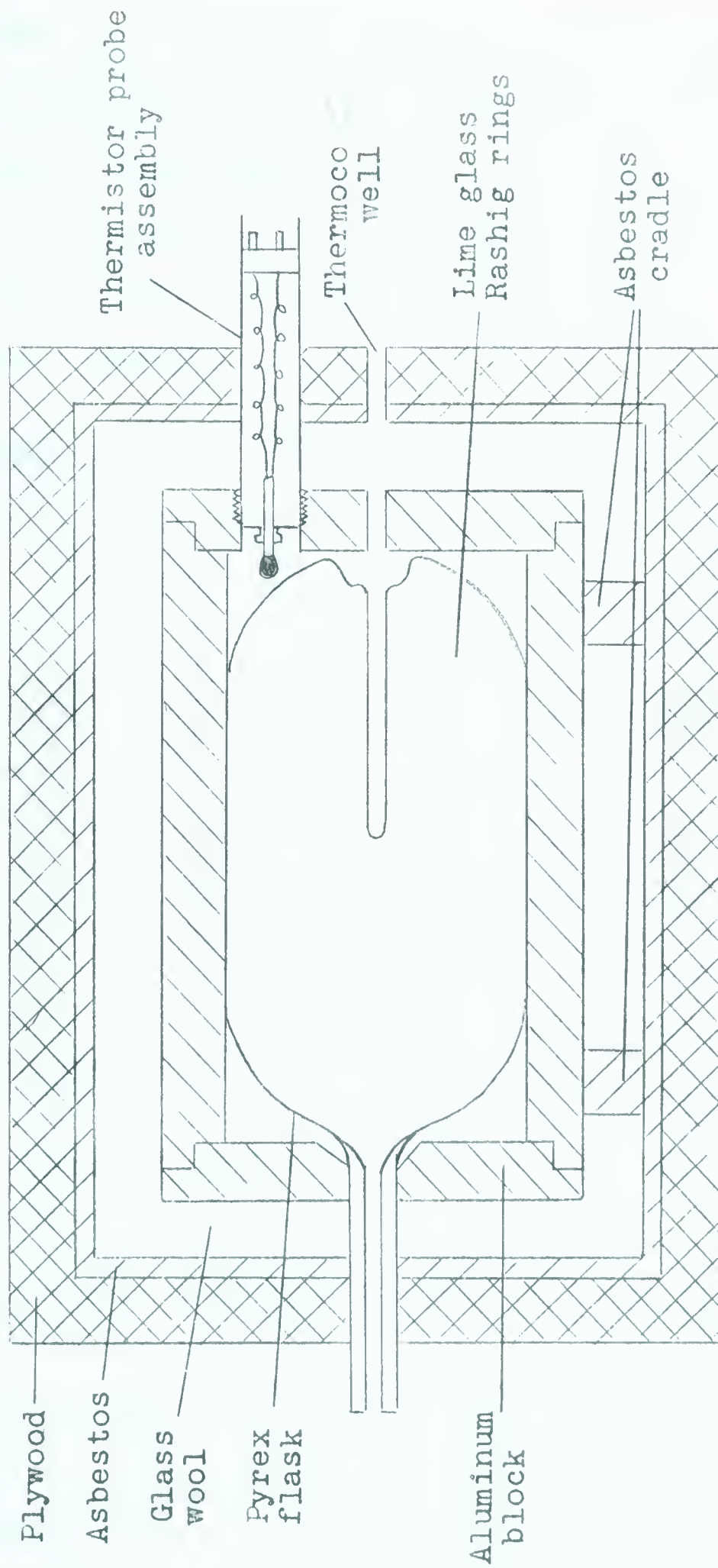


Fig. 5 Packed Reactor #2

time. Most of the runs carried out in this reactor were of 5 minutes duration, so no appreciable error was introduced due to this simple temperature control. It was found that when the reactor was maintained at 160°C the surface of the outer box was quite cool to the touch and the two thermocouples gave virtually identical readings.

Packed Reactor #1: This consisted of a 500 cc. pyrex bulb filled with Rashig rings made from 6 mm. O.D. x 3 mm. I.D. lime glass tubing. The volume remaining was found experimentally to be 326 cc.. Calculations made on the dimensions of the Rashig rings and the average size of a number of them taken at random gave a value for the surface area of 9.22 sq. cm./gm.. The total internal surface area of the reactor was calculated to be 306 sq. cm. and so the unpacked reactor #1 had a surface/volume ratio approximately 16 times that of the unpacked reactor. The reactor was immersed in a bath of molten wax maintained at 158°C by means of a tubular electric heater which was supplied with current by a Sorensen voltage regulator and a Powerstat autotransformer. An electric stirrer and a mercury in glass thermometer also dipped into the heating liquid. It was found that the wax became very dark after a short time and although a cover was fitted to the bath with holes cut to admit the various pieces of equipment only and the laboratory was well ventilated, the faint odour of the hot wax proved nauseating to workers who spent long periods in the laboratory. For this reason the more elaborate electrically heated packed reactor #2 was constructed.

Packed Reactor #2: This was a cylindrical pyrex vessel with hemispherical ends packed with lime glass Rashig rings of the type described previously to give a surface/volume ratio about 20 times that of the unpacked reactor. The mouth of the vessel was drawn down to 3 mm. capillary tubing and a thermocouple well extending to the centre of the vessel was attached to the centre of the closed end. The vessel was wrapped in aluminum foil and enclosed in an aluminum cylinder with detachable ends. The free space at each end was packed with aluminum foil. The cylinder was wrapped with asbestos paper and two separate nichrome heating elements were wound on top of this, being insulated from each other by a layer of asbestos paper. The assembly was mounted on an asbestos cradle and enclosed in an asbestos-lined plywood box. The space between the cylinder and the box was packed with glass wool. A thermistor assembly for use with a Sargent Thermonitor thermoregulator, originally designed for use in liquid media, was adapted to fit in the end plate of the aluminum cylinder so that the thermistor protruded into the foil-packed space around the pyrex vessel. The heating elements were connected to a Sargent Thermonitor, one being used as a base heater and the other as an intermittantly powered control heater. A rheostat was wired in series with the control heater as a ballast resistor and adjusted so that the total resistance of the circuit reached the value required for the correct operation of the Thermonitor. This arrangement gave a temperature variation, as measured by an iron/constantan thermocouple, of considerably less than 0.5 centigrade degrees over several weeks.

In some later runs the packed reactor #2 was modified by

replacing the packing with Rashig rings made from pyrex and of quartz of the same dimensions as the lime glass originally used. For ease of changing packings it was finally fitted with a greaseless "Asco seal" ground glass stopper which utilised a silicone rubber gasket for sealing. To accomodate this the furnace was lengthened.

Gas Chromatographic Apparatus.

A Gow-Mac thermal conductivity cell using hot wire sensors was attached to an aluminum preheater block and the assembly enclosed in a glass wool packed asbestos box. It was maintained at approximately 65°C by means of a heating element wound around the block and the bridge current was supplied by a Gow-Mac power Supply Control Unit. Hydrogen which was dried by passing it through a silica gel column was used as carrier gas and the flow rate was maintained at 50 cc./min..

After passing through the measuring side of the thermal conductivity cell, the gas stream could be diverted through a removable trap which could be cooled in liquid nitrogen. By this means any peak could be trapped out and analyzed on the mass spectrometer or rerun on another column. Before being exhausted into a fume cupboard, the gas stream flowed through an Octoil-S in glass flowmeter which was calibrated using a soap bubble flowmeter.

For measurement of ethane, DTBP, vinyl chloride, acetone, isobutylene oxide, tertiary butanol and isobutyraldehyde a 1½ m. glass enclosed column of β,β -oxydipropionitrile on Burrell kromat F.B. maintained at 25°C was found to be satisfactory.

TABLE III

Retention Times (Minutes) for Various Compounds encountered in This Investigation on several of the Columns Used.

All columns were about $1\frac{1}{2}$ metres long and the carrier gas was hydrogen. A flow rate of about 50 cc. per minute was maintained in all cases and the support medium was a proprietary brand of firebrick except in the case of alumina which requires no support.

Compound	β,β -oxy-dipropio-nitrile 25°C	Didecyl-phthalate 25°C	Tri-cresyl Phosphate 25°C	"Ucon"/ "Octoil-S" 25°C	Alumina 25°C-200°C (programmed)
Air	0.52	0.73	0.56	0.50	0.66
Ethane	0.52	0.73		0.76	1.95
Ethylene	0.52				3.58
Propane	0.52				5.69
Propylene	0.52			1.22	8.68
n-Butane					9.86
iso-Butylene	12.22				
n-Hexane					16.60
Vinyl Chloride	1.04	2.12		3.34	
2-Chlorobutane	4.53	20.65	10.79		
Acetone	21.86	9.49	9.66		
Isobutylene Oxide	9.46				
Isobutyraldehyde	13.81				
Tert-Butanol	24.20				
Di-Tert-Butyl Peroxide	4.49	56.90	25.16		

TABLE IV

Gas Chromatographic Sensitivities for Compounds Measured
Quantitatively During This Investigation.

Compound	Sensitivity (molecules, cm ⁻² x 10 ⁻¹⁶)
Ethylene	4.66
Propylene	3.55
n-Butane	2.63
n-Hexane	1.84
Vinyl Chloride	2.79
2-Chlorobutane	1.35
Acetone	2.60
Isobutylene Oxide	4.62
Tert-Butanol	2.20
Di-Tert-Butyl Peroxide	2.16
Ethane: Sensitivity as peak height on $\beta\beta$ -oxydipropionitrile column under the conditions used in kinetic runs = 6.09×10^{15} molecules, cm. ⁻¹	

The values listed above are absolute sensitivities calculated from repeated determinations made over a short period of time early in the investigation. While the relative sensitivities did not change appreciably during the investigation the absolute values were repeatedly corrected from time to time by redetermining values for acetone or peroxide and ethane and recalculating the sensitivities of the others by proportion.

Retention times for these compounds will be found together with their sensitivities in Tables III and IV (pages 30 and 31).

It will be noted that ethane is not retained by the β,β -oxydipropionitrile column but coincides with the air peak. The sensitivity for ethane is given as a peak height and several calibration runs for ethane showed that this is a sufficiently reproducible procedure. Care was taken in all runs to exclude air from the sample and no appreciable error could be expected to be introduced through its presence. In several preliminary runs the ethane/air peak was trapped in liquid nitrogen and rerun on a $1\frac{1}{2}$ m. alumina column whose temperature was programmed steadily from 25°C to 200°C. The amounts of ethylene, propane and propylene detected by this method were in all cases so much less than the ethane as to make correction of the ethane peak height for these compounds unnecessary.

Peak areas as measured by a planimeter were used to determine the sensitivities and hence the quantities of the other compounds. A $1\frac{1}{2}$ m. tricresyl phosphate on Columpak column at 25°C was used to separate 2-chlorobutane from the other components. On the β,β -oxydipropionitrile column the DTBP masked the 2-chlorobutane both having similar retention times.

In the preliminary experiments with the DTBP/ethylene system ethane, ethylene, propane, propylene, n-butane and n-hexane were separated on an alumina column programmed from 25°C to 200°C.

RESULTS AND DISCUSSION

Methyl Radical Addition to Ethylene.

Before studying the vinyl chloride system it was thought that it would be worthwhile to repeat Brinton's work with ethylene. This would serve the double purpose of gaining experience and also checking the reproducibility of Brinton's results.

Such a study on ethylene was performed and during it several experimental techniques were tried until a satisfactory one was arrived at. The experimental procedure which was finally adopted has already been described in the Experimental section and was used also for the vinyl chloride investigation. The only major differences between the two sets of experiments were that in the ethylene experiments the peroxide concentration was kept only very approximately constant from run to run while in the vinyl chloride experiments the use of a metal stopcock on the peroxide reservoir allowed much better control of the amounts of peroxide used. The analysis of the ethylene system was confined to ethane, ethylene, propane, propylene, n-butane and n-hexane.

The results were treated in the manner developed by Brinton (See page 19) and are tabulated in Table V (page 34).^{*} Figs. 6 and 7 (pages 35 and 36) show a plot of $(RC_4H_{10} + 2.26RC_6H_{14})/RC_2H_6$ ^{1/2} versus ethylene concentration and the derived Arrhenius plot respectively.

* Rates of formation of propane and propylene are not listed here but will be discussed later in this chapter.

TABLE V

Rates of Product Formation in Methyl Radical/Ethylene Reaction.

Run No.	Ethylene Conc. (a)	RC_2H_6 (b)	RC_4H_{10} (b)	RC_6H_{14} (b)	$\frac{\text{RC}_4\text{H}_{10} + 2.26\text{RC}_6\text{H}_{14}}{\text{RC}_2\text{H}_6^{\frac{1}{2}}}$ (c)	Temp. (°C)	Reaction Time (min.)
60	132	8.38	4.01	0.735	0.62	124.0	180
59	221	7.17	5.39	1.40	1.01	124.0	180
58	231	9.53	6.11	1.67	1.02	124.0	180
57	312	4.45	4.82	2.35	1.52	124.0	180
56	374	7.62	7.01	3.44	1.69	124.0	180
39	239	124	44.0	6.53	1.67	140.0	30
33	260	123	46.4	5.98	1.71	140.0	30
30	298	146	51.4	9.75	1.90	140.0	30
38	410	103	60.5	12.9	2.80	140.0	30
40	494	105	62.0	17.2	3.11	140.0	30
34	686	83.5	67.5	26.3	4.39	140.0	30
46	231	814	157	14.6	2.11	158.5	5
49	349	664	234	29.0	3.68	158.5	5
48	398	622	231	35.6	3.94	158.5	5
44	441	906	284	61.6	4.45	158.5	5
47	513	581	280	59.5	5.45	158.5	5

(a) molecule $\text{cm}^{-3} \times 10^{-15}$

(b) molecule $\text{cm}^{-3}\text{sec}^{-1} \times 10^{-11}$

(c) molecule $^{-\frac{1}{2}}\text{cm}^{-\frac{3}{2}}\text{sec}^{-\frac{1}{2}} \times 10^{-6}$

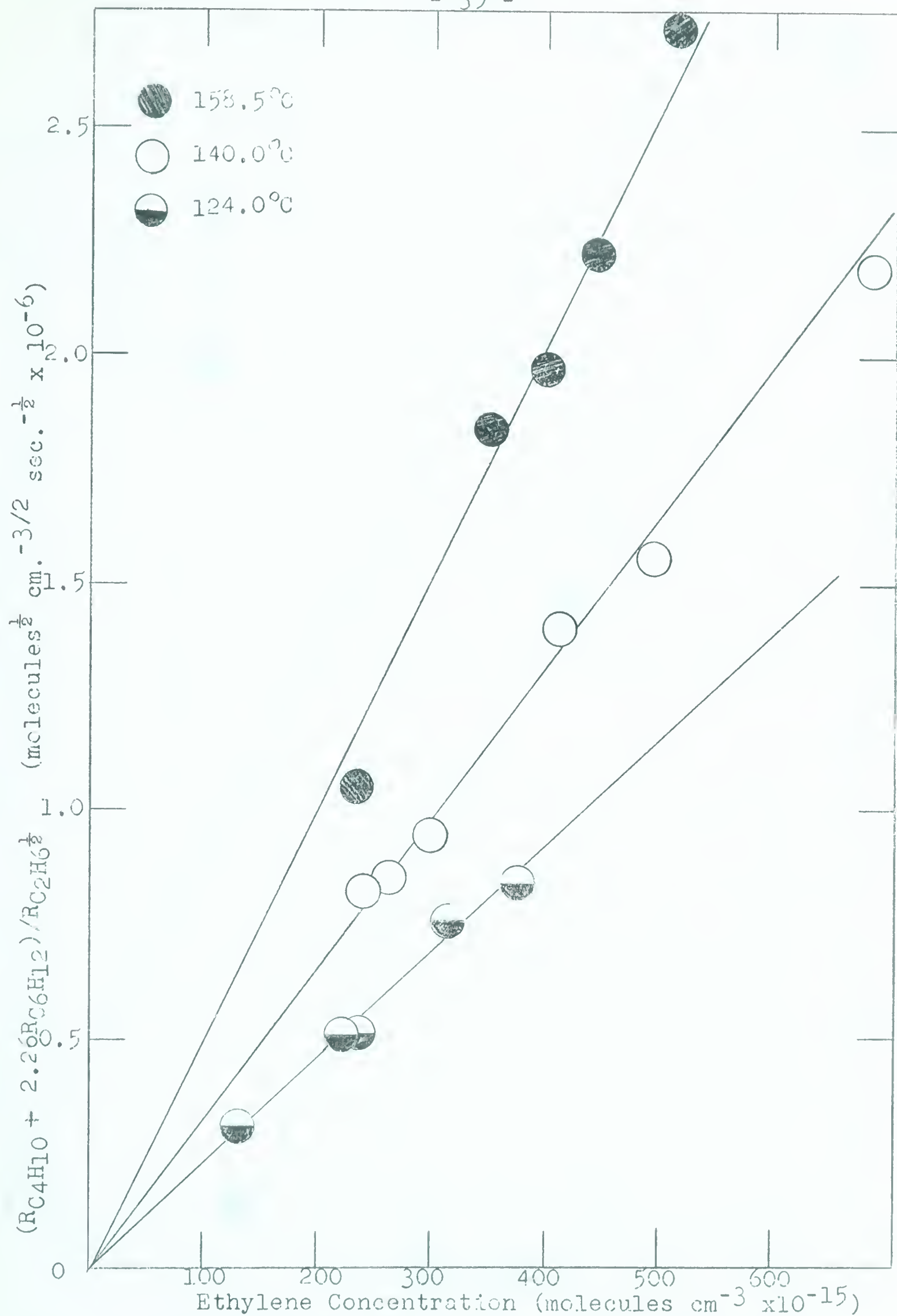


Fig. 6 Kinetic plot of data in methyl radical/ethylene reaction.

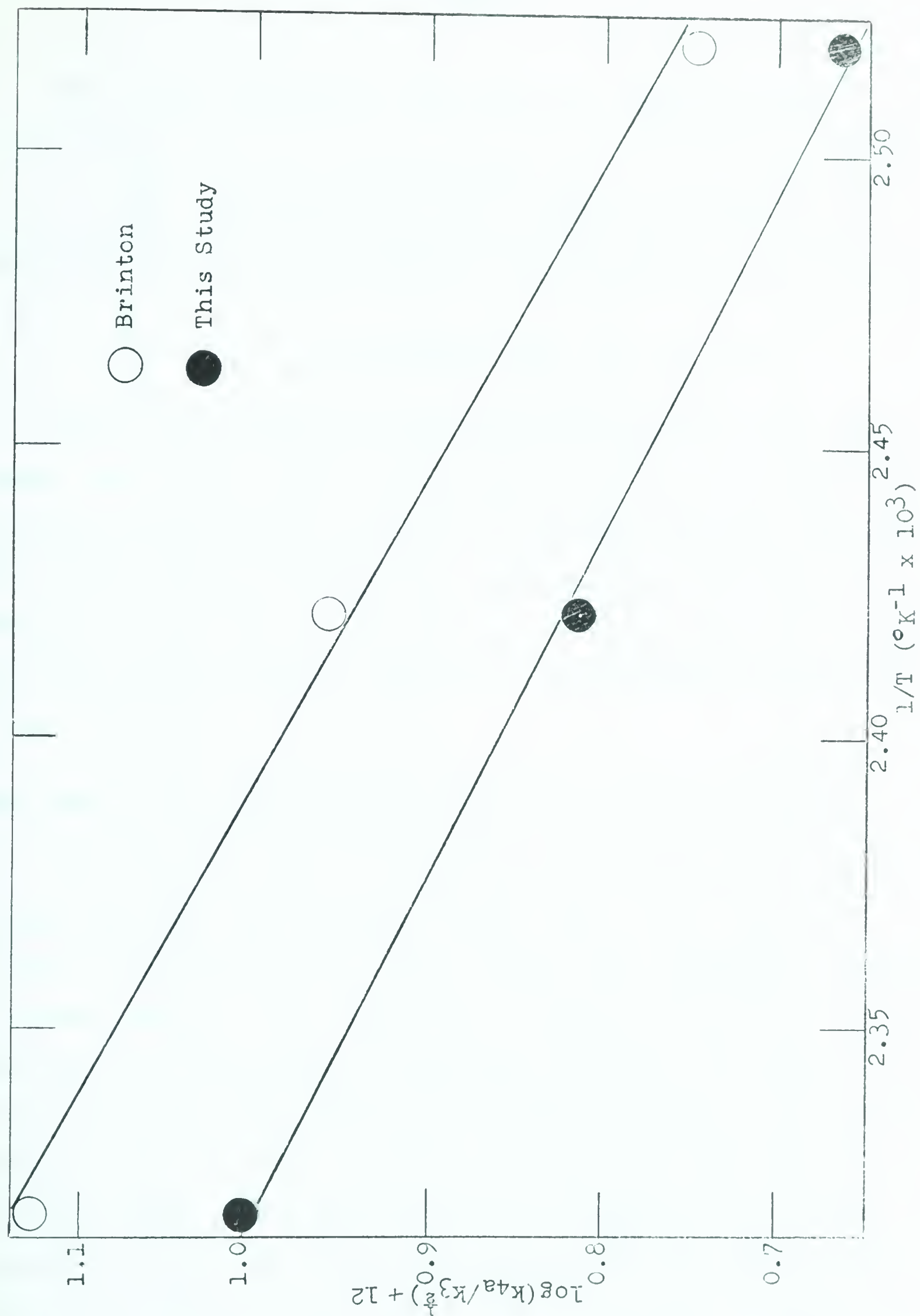


Fig. 7 Arrhenius plot for $k_{4a}/k_3^{1/2}$ in $CH_3./C_2H_4$ reaction.

The values obtained for the Arrhenius parameters are:

$$\frac{k_{4a}}{k_3^{\frac{1}{2}}} = 0.904 \times 10^{-7} e^{-7820/RT} \text{ cm}^3 \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$$

which are in fairly good agreement with Brinton's

$$\frac{k_{4a}}{k_3^{\frac{1}{2}}} = 3.3 \times 10^{-7} e^{-8860/RT} \text{ cm}^3 \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$$

While the precision of this preliminary work was not very great, the lessons learnt from the difficulties encountered therein could be applied to the study of the vinyl chloride reaction. One further item of interest does however emerge from the data obtained in this series of experiments namely a means of calculating the relative rates of combination and disproportionation of propyl radicals.

The Combination and Disproportionation of n-Propyl Radicals.

In Brinton's study of the methyl radical/ethylene reaction propyl radicals are assumed to either add a methyl radical to butane, disproportionate to give propane and propylene or combine to give n-hexane. The n-butane and n-hexane were measured quantitatively but the propane and propylene were not. The amount of propyl radicals disappearing by disproportionation is calculated from the rate of hexane formation by using the value for the relative rates of disproportionation to combination of propyl radicals of 0.13 determined by Whiteway and Masson (25) in the photolysis of di-n-propyl ketone. In the present investigation propane and propylene could both be determined quantitatively on

TABLE VI

Rates of Production of Propane, Propylene and n-Hexane in Methyl Radical/Ethylene Reaction.

Ethylene Pressure (mm.)	R _{propane}	R _{propylene} (arbitrary units)	R _{n-hexane}
6.3	8.5	11.3	26.8
7.3	1.7	6.0	7.3
10.9	6.2	13.5	38
11.0	2.6	7.9	13.7
11.1	5.7	8.3	29.3
12.0	5.9	13.0	32.5
12.3	2.8	9.2	16.4
14.2	6.2	13.3	43
15.0	17.9	17.5	82.0
17.4	4.2	12.1	25.2
17.6	17.9	16.0	79.6
18.7	11.4	18.1	76
20.6	5.2	12.7	32.5
21.2	19.4	18.8	85.4
22.5	8.2	18.1	64
23.8	15.1	22.9	96
24.2	14.2	22.4	90.0
24.6	12.8	21.0	75
25.4	7.7	16.8	56.0
27.3	26.8	18.8	77.0
28.8	15.4	27.2	69.0
29.1	18.2	26.0	111
31.0	12.6	23.2	98
32.0	17.2	25.2	123

the alumina column used. The peaks corresponding to these products were, however, small and the error in measurement is therefore significant. If we consider a large number of runs and treat them statistically, a fairly accurate value should be obtained.

In Table VI (page 38) values for the rates of formation of propane, propylene and n-hexane from all the runs made, including many preliminary runs where, for one reason or another, complete analysis was not made or the absolute sensitivity of the gas chromatography apparatus was not known accurately. The relative sensitivities for the three compounds in any one run will of course be identical but the actual rates listed are in arbitrary units (approximately molecules/cc.sec. $\times 10^{-11}$). Most of the runs are at 158.5°C and the actual ethylene concentrations used in each run is included in the table.

One striking feature of these data is that in almost all cases the propylene formed is more than the propane formed and if we consider the sums of the rates of formation of these compounds over all the runs we find:

$$\frac{\sum R_{\text{propylene}}}{\sum R_{\text{propane}}} = 1.50$$

It appears therefore that there is some other source of propylene besides the disproportionation of two propyl radicals. The excess propylene could perhaps be explained by a disproportionation between methyl and propyl radicals.



There is always a small amount of methane present in the decomposition products of DTBP and this was not significantly increased when ethylene was added to the system. However, only a very slight increase in the methane production would be required to explain the excess of propylene over propane. The expected increase is essentially within the experimental error and thus no attempt was made to measure it.*

While the origin of the propylene is not clear, it is hard to account for the production of propane other than by the disproportionation of propyl radicals. If we therefore assume that this is the case, the disproportionation/combination ratio will be given by:

$$\frac{\text{Rate of propane production}}{\text{Rate of n-hexane production}}$$

In Table VI (page 38) this is calculated for each run and the median value of these results is 0.168.

This is in relatively good agreement with previously published values. (See Table VII, page 41).

* In an experiment which will be discussed later in which fully deuterated vinyl chloride was used in place of ethylene, undeuterated propylene was found among the products. (See page 63.) Since there is no propylene formed in the decomposition of DTBP alone it is difficult to advance an explanation for this result.

TABLE VII

Literature Values for n-Propyl Radical
Disproportionation/Combination Ratio.

			<u>Reference</u>
(1)	Kerr & Calvert	0.157	(26)
(2)	Kerr & Trotman-Dickenson	0.16	(27)
(3)	Ausloos & Murad	0.148 0.152 0.155 0.187	(28)
(4)	Whiteway & Masson	0.13	(25)
(5)	Masson	0.21	(29)
(6)	Blacet & Calvert	0.1	(30)
(7)	Caule & Steacie	0.3	(31)
(8)	This Study	~ 0.17	

Thermal Decomposition of DTBP in the Presence of Vinyl Chloride.

In order to study the addition of methyl radicals to vinyl chloride, experiments were undertaken in which the ethylene was replaced with vinyl chloride. It was hoped that by collecting corresponding products, an interpretation of the results analagous to that with ethylene would be feasible. It soon became clear that the vinyl chloride system behaves anomalously. Addition of vinyl chloride increased the acetone yield and caused the formation of significant amounts of two new products, methane and isobutylene oxide.

The rates of formation of the major products in runs performed

at 158.5°C are shown in Table VIII (pages 43 and 44) and plotted as functions of vinyl chloride concentration in Fig. 8 (page 45).

It will be remembered that in the ethylene system the rate of methane production never increased appreciably over the small value observed in the decomposition of pure DTBP and the rate of acetone formation was unaffected by added ethylene. Isobutylene oxide was not found as a product in the ethylene/DTBP reaction although trace quantities were probably formed.

A noticeable feature of the rates of product formation in the vinyl chloride reaction is that the increase in rates of formation of methane, isobutylene oxide and acetone are parallel so the approximate equality below is observed.

$$R_{CH_4} \sim R_{\text{isobutylene oxide}} \sim \Delta R_{\text{acetone}}$$

(where $\Delta R_{\text{acetone}}$ is the increase in the rate of acetone formation over that found in the decomposition of pure DTBP)

This immediately suggests that the vinyl chloride in some way "sensitizes" the further decomposition of the DTBP according to the overall reaction



A clue to the mechanism of this effect was obtained from the work of Raal and Steacie (32) dealing with the photolysis of acetone in the presence of methyl chloride, methylene dichloride and chloroform. They found that methane was a major product of the reaction and its rate of production increased from methyl chloride through

TABLE VIII

Rates of Product Formation in Methyl Radical/Vinyl Chloride Reaction

in Unpacked Reactor and in Packed Reactor #1.

Run	Vinyl Chloride Conc. (a)	Residual Peroxide Conc. (a)	R_{CH_4} (b)	$R_{C_2H_6}$ (b)	$R_{isobutylene oxide}$ (b)	$R_{acetone}$ (b)	$\frac{R_{CH_4} + 2R_{C_2H_6}}{R_{acetone}}$	$\frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}}$ (c)
1	0	185	1.95	95.5	9.14	167	1.2	--
2	0	185	2.43	94.5	25.4	146	1.3	--
3	4.18	177	12.1	77.9	79.2	149	1.3	4.78
4	6.07	171	39.0	78.5	78.4	181	1.1	4.41
5	6.66	180	25.9	98.9	36.0	174	1.3	2.61
6	7.06	---	16.6	90.2	66.1	155	1.3	1.75
7	10.7	177	38.6	63.2	71.6	153	1.1	4.92
8	20.6	165	64.4	83.5	105	193	1.2	7.06
9	22.7	159	94.0	43.3	141	210	0.86	14.3
10	28.9	171	85.9	57.2	87.4	184	1.1	11.3
11	44.1	160	126	65.9	129	213	1.2	15.4
12	54.2	155	118	48.6	130	238	0.90	16.9
13	132	152	140	36.8	152	230	0.93	23.1
14	237	160	136	33.6	97.7	256	0.79	23.5
30	244	151	104	29.3	110	260	0.63	19.6

TABLE VIII - Continued

Reaction with added amine (C ₂ H ₅) ₃ N						
22	9.85	---	21.1	--	---	--
21	10.4	178	14.7	58.5	66.4	164 0.81
20	121	169	52.1	25.0	88.8	193 0.53
Reaction in packed reactor #1						
24	0	186	5.28	95.2	0	175 1.12
25	20.8	189	6.04	82.8	0	173 0.99
26	168	184	5.59	44.8	0	183 0.52

(a) molecule $\text{cm}^{-3} \times 10^{-15}$

(b) molecules $\text{cm}^{-3} \text{sec}^{-1} \times 10^{-12}$

(c) molecules $\frac{1}{2} \text{cm}^{-2} \times 10^{-6}$

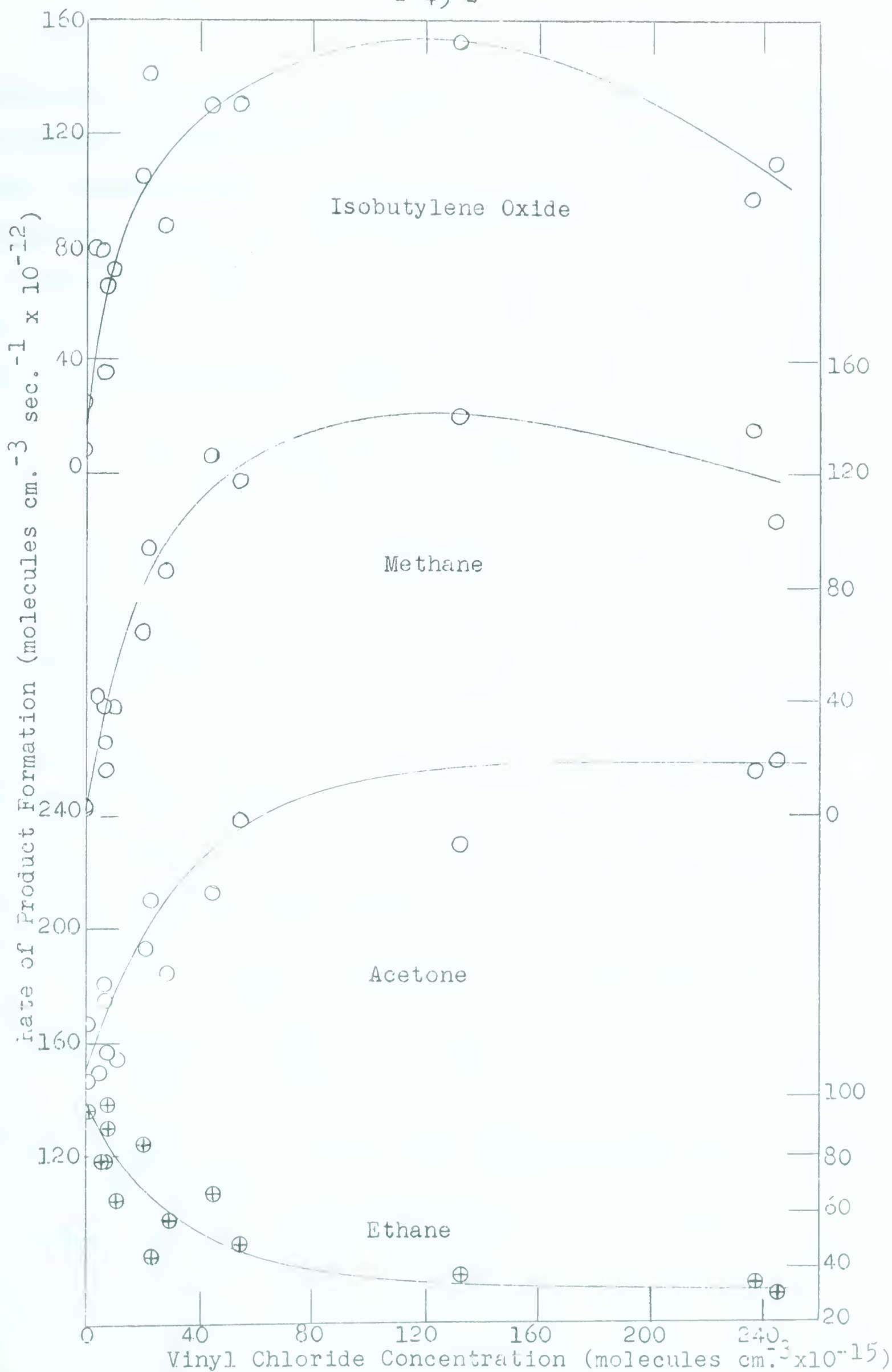
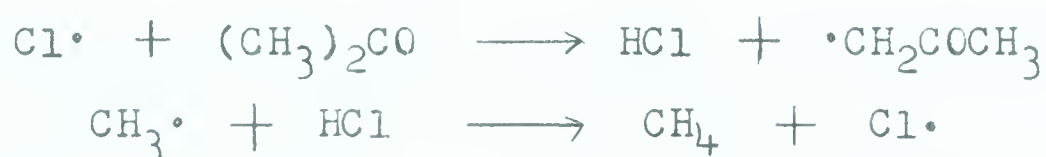


Fig. 8 Rates of product formation in $\text{CH}_3./\text{CH}_2\text{CHCl}$ reaction

methylene dichloride to chloroform. They at first assumed this to be due to hydrogen abstraction from these compounds but when carbon tetrachloride was studied (33) the rate of production of methane was found to be even greater than that with chloroform.

Cvetanović, Raal and Steacie (33) concluded that the explanation of the effect lay in the formation of chlorine atoms by some obscure mechanism followed by the reaction sequence:



Further studies by the same group (34), where HCl was added to the acetone before photolysis, showed that methane was produced in large quantities as would be expected if the above mechanism is correct. The abstraction of hydrogen by methyl radicals from HCl was found by these workers to be extremely rapid and they calculated that the activation energy was as low as 2 kcal./mole.

If we compare this rate with that of addition of methyl to ethylene at similar temperatures:

$$\text{Cvetanovic et al. } \left(\frac{k_1}{k_2^{\frac{1}{2}}} \right)_{150^\circ\text{C}} \sim 4.5 \times 10^{-9} \text{ cm}^{\frac{3}{2}} \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$$



$$\text{Brinton } \left(\frac{k_{4a}}{k_3^{\frac{1}{2}}} \right)_{158^\circ\text{C}} \sim 13 \times 10^{-12} \text{ cm}^{\frac{3}{2}} \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$$



We see that the rate of hydrogen abstraction from HCl is faster by a factor of about 10^3 . Thus very small traces of HCl of the order of 0.1% would be expected to have a profound effect on the course of the reaction in a system where methyl radicals and an olefin are present.

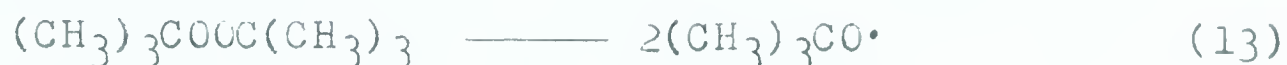
Cvetanović, Raal and Steacie (33) photolysed acetone in the presence of CCl_4 at room temperature where ammonia had been added to the system and showed that the production of methane was almost completely suppressed, indicating that HCl was present in the reaction mixture. Attempts to suppress the formation of methane at high temperatures by addition of ammonia failed, presumably due to the thermal dissociation of ammonium chloride.

Cvetanović and Steacie suggested that the production of chlorine atoms in the photolysis of acetone and chlorinated methanes might be due to an acetone photosensitized decomposition of the chlorinated methanes.

A further clue to the course of the vinyl chloride/DTBP reaction comes from the work of Bose and Hinshelwood (35) who, in continuing the study of the catalytic influence of foreign gases on the thermal decomposition of DTBP which had been begun by Birss (36), noted that carbon tetrachloride had a very marked effect on the decomposition. While other gases had been found to increase the rate of decomposition of the peroxide without affecting the product distribution, carbon tetrachloride markedly altered this. In particular methane became a major product and the rate of acetone formation was greatly increased. Methyl ethyl ketone was reported as a major product but it appears that it was in fact isobutylene

oxide which was observed.* A similar effect was found with silicon tetrachloride and it was suggested that chlorine atoms may be formed during this reaction but no further explanation was advanced.

One other earlier investigation is of interest in its similarity to the present problem, namely the work of Raley, Rust and Vaughan (37). These authors noted that the addition of HCl to ethylene in the gas phase is catalyzed by the addition of DTBP and they suggest that the reaction scheme:



accounts for the initiation step. However they did not analyze the reacted mixture for tert. butanol or isobutylene oxide.

Considering the vinyl chloride reaction in the light of these earlier investigations, it appears that a very similar phenomenon is occurring and it seems likely that HCl is being formed in the reaction. If this is the case then it should be possible to detect its presence and a variety of experimental techniques were applied to this end.

* Their means of identification was by mass spectrometry alone. In an experiment performed during this work where DTBP and CCl_4 were reacted together isobutylene oxide was found as a product but no methyl ethyl ketone. Both gas chromatography and mass spectrometry were used in the identification and while the mass spectra of the two compounds are remarkably similar, methyl ethyl ketone is very strongly retained by a β,β -oxydipropionitrile column while isobutylene oxide is not.

Detection of HCl in Reaction Mixture.

(a) In several runs where about 15 mm. of vinyl chloride had been present in the reaction mixture (this corresponds to about 250×10^{15} molecules/cc. in the reactor and is equivalent to the highest concentrations of vinyl chloride used in the kinetic runs) the products were condensed together with approximately 2 cc. of aqueous silver nitrate solution by cooling with liquid nitrogen in a sidearm attached to bulb D. On warming a slight white precipitate which darkened in the light was found to be present. Identical treatment of the unreacted mixture (corresponding to about four times the amount recovered after reaction) produced no such precipitate.

(b) In similar experiments 2 cc. of distilled water was used in place of the silver nitrate solution and the pH of the resulting solution determined using a Beckmann expanded scale pH meter and a teflon block so designed that 2 cc. of solution was adequate to immerse both the glass electrode and the reference electrode. In these experiments the control samples consisted of approximately $\frac{1}{4}$ of the unreacted mixture in bulb C frozen down in 2 cc. of water.

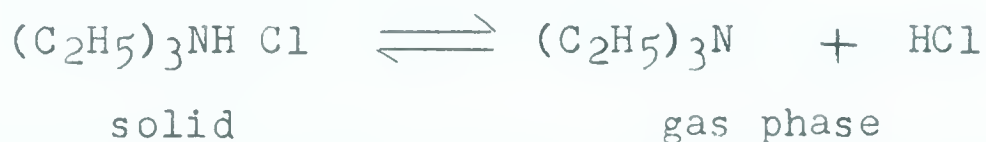
The results for two such runs were:

	(a)	(b) *
pH of Distilled water	5.92	5.40
pH of Unreacted Mixture	4.52	4.10
pH of Reacted Mixture	3.50	3.20

* For quantitative exploitation of these results see page 51.

(c) If the HCl does in fact catalyze the reaction, then the addition of an amine to the reaction mixture might remove the HCl and thereby alter the distribution of the products. The amine hydrochloride can be expected to have a higher thermal stability than the ammonium chloride in the experiments of Cvetanović et al. (33). Some runs were performed in which triethylamine was added to the reaction mixture and the results are shown in Table VIII. It can be seen that, while the production of methane is not halted, it is significantly reduced (by a factor of about 2) from that in comparable runs without added amine.

The failure to completely suppress the reaction is probably due to the thermal dissociation of the amine salt.



It seems safe to conclude from these observations that HCl is in fact present among the reaction products.

An investigation of the gas phase HCl catalyzed decomposition of DTBP by Benson and co-workers (38) published after this work was completed examined the reaction at much higher (one or two orders of magnitude) HCl concentrations. While the reaction products are quite similar, Benson finds that the induced decomposition of the DTBP is independent of the HCl concentration. The present results show that the induced decomposition is dependent on the amount of chlorine containing compound and thus presumably on the HCl concentration. This difference in behaviour is not unexpected considering the difference in conditions in the two systems.

Concentration of HCl in the Reaction System.

It is possible to obtain three independent estimates of the HCl concentration in the reaction system. The first method is based on the pH measurements quoted on page 49.

Concentration of vinyl chloride = 250×10^{15} molecules/cc.

Concentration of H ions in 2 ml water = $10^{-3.3}$ gram ions/l.

$$\begin{aligned} \text{Therefore number of H ions} &= \frac{5.0 \times 10^{-4} \times 6 \times 10^{23} \times 2}{10^3} \\ &= 6.0 \times 10^{17} \text{ H ions} \end{aligned}$$

"Effective"* volume of unpacked reactor = 333 cc.

$$\begin{aligned} \text{Therefore concentration of HCl} &= \frac{6 \times 10^{17}}{333} \text{ molecules/cc.} \\ &= 1.8 \times 10^{15} \text{ molecules/cc.} \end{aligned}$$

The second estimate is obtained from a calculation of the concentration of HCl from the kinetics of the reaction using the Arrhenius parameters determined by Cvetanović and Steacie (34).

Considering the reactions:



$$R_{\text{CH}_4} = k_7(\text{CH}_3\cdot)(\text{HCl})$$

$$R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} = k_3^{\frac{1}{2}}(\text{CH}_3\cdot)$$

* As explained on page 20, the reaction is terminated by allowing the reaction mixture to expand into bulb D (volume approximately 2 l.). Thus not all of the reaction mixture is recovered. It is convenient to imagine that the reactor is in fact slightly smaller and that the whole of the mixture is removed for analysis. This "effective" volume was calculated from blank experiments with relatively high pressures of air where the amount recovered was measured on the Toepler pump/gas burette.

$$\frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}} = \frac{k_7}{k_3^{\frac{1}{2}}} (HCl)$$

We require $\frac{k_7}{k_3^{\frac{1}{2}}}$ at 158.5°C.

From Cvetanovic' and Steacie $\frac{k_7}{k_3^{\frac{1}{2}}}$ at 150°C = 4.5×10^{-9}

$$E_7 = 2100 \text{ cal/mole}$$

$$E_3 = 0$$

and therefore

$$\left(\frac{k_7}{k_3^{\frac{1}{2}}} \right)_{159^\circ C} = 4.5 \times 10^{-9} e^{\frac{2100}{1.98 \times 423}} - \frac{2100}{1.98 \times 432}$$

$$= 4.6 \times 10^{-9}$$

$$\text{Therefore } (HCl) = \frac{R_{CH_4}}{R_{C_2H_6}} \times \frac{1}{(4.6 \times 10^{-9})}$$

$$\text{In plateau region } \frac{R_{CH_4}}{R_{C_2H_6}} \sim 30 \times 10^6$$

$$\text{Therefore } (HCl) = \frac{24 \times 10^6}{4.6 \times 10^{-9}}$$

$$= 6.5 \times 10^{15} \text{ molecules/cc.}$$

The third estimate is based on a kinetic interpretation of several runs (numbers 16 - 19 in Table IX, pages 53 and 54) made in the unpacked reactor with HCl in place of vinyl chloride.

In Fig. 9 (page 55) the ratio $R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}$ is plotted against

Rates of Product Formation in Reactions of Methyl Radicals with HCl in Unpacked and Packed Reactors and with Carbon Tetrachloride, Tetrachloroethylene and Chlorine in Unpacked Reactor.

Run No.	Substrate Conc. (a)	Residual Peroxide Conc. (a)	R_{CH_4} (b)	$R_{C_2H_6}$ (b)	$R_{isobutylene oxide}$ (b)	$R_{isobutyraldehyde}^*$ (b)	$R_{acetone}$ (b)	$\frac{R_{CH_4} + 2R_{C_2H_6}}{R_{acetone}}$
HCl in unpacked reactor.								
16	3.66	13.7	16.3	68.3	22.4	6.1	136	1.1
17	11.9	6.9	220	21.8	135	8.1	201	1.3
18	23.3	4.4	249	9.9	155	13.8	228	1.2
19	24.7	7.7	258	11.4	200	17.4	294	0.96
HCl in packed reactor #1.								
27	9.25	-	101	--	-	--	-	-
28	18.0	-	199	45.7	7.8	115	293	0.99
29	235	-	293	--	-	81.2	-	-
CCl_4 in unpacked reactor.								
23	12.3	17.9	16.6	78.9	40.0	0	177	0.98
CCl_2CCl_2 in unpacked reactor.								
15	91.5	14.2	116	43.4	175	16.0	190	1.1
Cl_2 in unpacked reactor.								
32	1.01	17.8	53.2	72.6	50.0	0	169	1.2
33	7.76	9.86	360	18.7	344	0.94	411	0.97

TABLE IX - Continued

(a) molecules $\text{cm}^{-3} \times 10^{-15}$

(b) molecules $\text{cm}^{-3}\text{sec}^{-1}$

All reactions were at 158.5°C and were of 5 minutes duration.

* Isobutyraldehyde appears as a noticeable product when HCl is used in place of vinyl chloride. Its rate of formation is greater in the packed reactor and it may be that an HCl catalyzed isomerization of the isobutylene oxide occurs on the glass surface. It was thought that isomerization might take place when the products are frozen down together prior to analysis but in experiments when isobutylene oxide and HCl were frozen down together and analysed, in conditions which duplicated those of a typical run, no aldehyde was found although a considerable proportion of the oxide was missing. It is believed that chlorohydrin formation is the explanation for this.

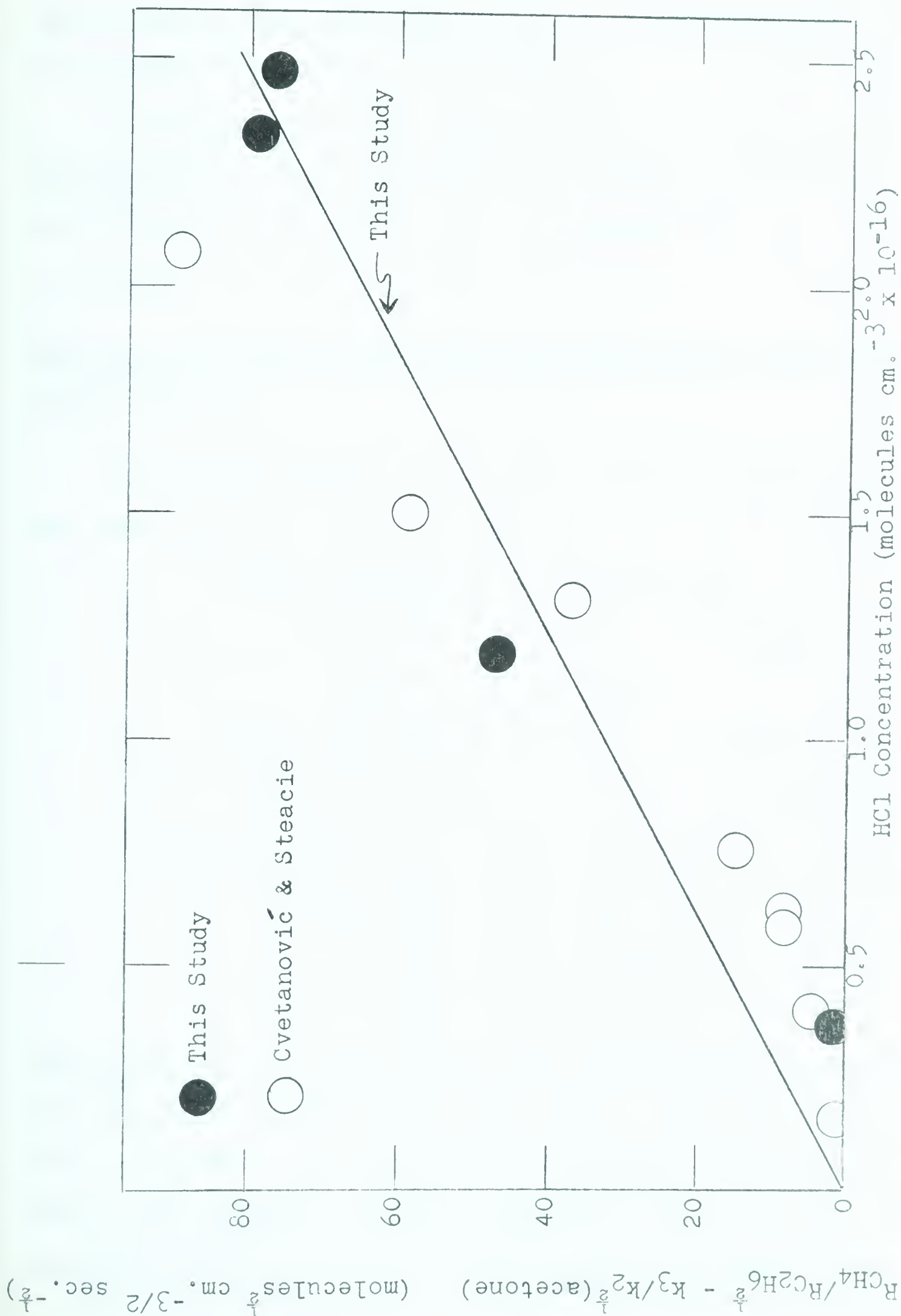


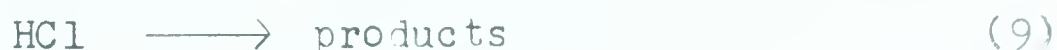
Fig. 9 Plot of $R_{CH_4}/R_{C_2H_6}^{1/2}$ versus HCl concentration in $CH_3./HCl$ reaction.

HCl concentration. In the plateau region of the vinyl chloride plot (Fig. 8, page 45) $R_{CH_4}/R_{C_2H_6}^{1/2} = 22 \times 10^6$ and this corresponds to an HCl concentration of approximately 6.8×10^{15} molecules/cc..

Considering the approximate nature of these estimates and the experimental errors inherent in the method of measurement of HCl concentration by means of pH, the agreement must be considered very good.

Reaction Mechanism of HCl Catalyzed Reaction in the Presence of Vinyl Chloride.

With this evidence it is now possible to propose a mechanism for the reaction. It is as follows:



Reactions (1), (2) and (3) are well established in the thermal decomposition of DTBP in the gas phase. Reactions (5) and (6) form a sequence that explains the observed formation of isobutylene oxide and increased acetone formation in the ratio 1:1. The same sequence was also assumed by Benson and co-workers (31). Reaction

(7) regenerates chlorine atoms for the chlorine atom chain and was sufficiently substantiated in the previous discussion. Reactions (4), (8) and (9) require further examination.

Release of Chlorine Atoms by Vinyl Chloride - Reaction (4) in Proposed Kinetic Scheme.

In considering the nature of reaction (4) it will be informative to examine the results of the runs made with carbon tetrachloride and tetrachloroethylene which are included in Table IX (pages 53 and 54). These runs were performed to confirm the supposition that any compounds of this general type will give rise to large amounts of methane and "sensitize" the decomposition of the DTBP when they are mixed with it before pyrolysis. Also it was necessary to show that the effect of adding carbon tetrachloride to DTBP before pyrolysis is identical with that of adding it to acetone before photolysis (33).

Examination of Table IX (pages 53 and 54) shows that both carbon tetrachloride and tetrachloroethylene cause very similar effects on the decomposition of DTBP as does vinyl chloride. In all cases a large increase in the rate of methane formation, appearance of isobutylene oxide as a major product and increased rate of decomposition of the peroxide, as evidenced by the greater quantity of acetone produced, are observed.* In particular in the case of the methyl radical/carbon tetrachloride system the effect

* Runs with chlorine in place of vinyl chloride (Table IX, page 53) also gave rise to methane and isobutylene oxide. Chlorine was found to rapidly attack the mercury manometers threatening to render them useless and so these runs were hurried and the data are of low precision.

observed appears to stem from the interaction of the radicals with the carbon tetrachloride so that the suggested (33) acetone photo-sensitized decomposition of the carbon tetrachloride is not required

The similarity between the reaction of methyl radicals with vinyl chloride, carbon tetrachloride and tetrachloroethylene being apparently due to the production of chlorine atoms from these compounds, it is of interest to compare the relative ease with which these compounds liberate a chlorine atom. An attempt to do this was made by plotting $R_{CH_4} / R_{C_2H_6}^{1/2}$ versus the concentration of the added chlorine containing compound (Fig. 10, page 59).

The plot contains, besides the present results with vinyl chloride, the results obtained by Cvetanovic and Steacie with carbon tetrachloride* (Table X, page 60). It is interesting to note that the points for all compounds fall on the same curve. Remembering that $R_{CH_4} / R_{C_2H_6}^{1/2}$ should be proportional to the concentration of HCl, the plot means that the steady state concentration of HCl is dependent only on the concentration but not the identity of the chlorine bearing compound.

This result is, at first, difficult to understand. If the steady state concentration of HCl is governed by its rate of production (4) and rate of removal (7) and (8), then it would be hard to conceive that for all the different systems the rates of these reactions should be the same. A plausible alternative is the assumption that the HCl concentration is in some way controlled by

* Cvetanovic and Steacie's data used for the plot are corrected to take into account the H abstraction by methyl radicals from acetone. They correspond to $CCl_4 \cdot (CCl_4)$ of reference (33).

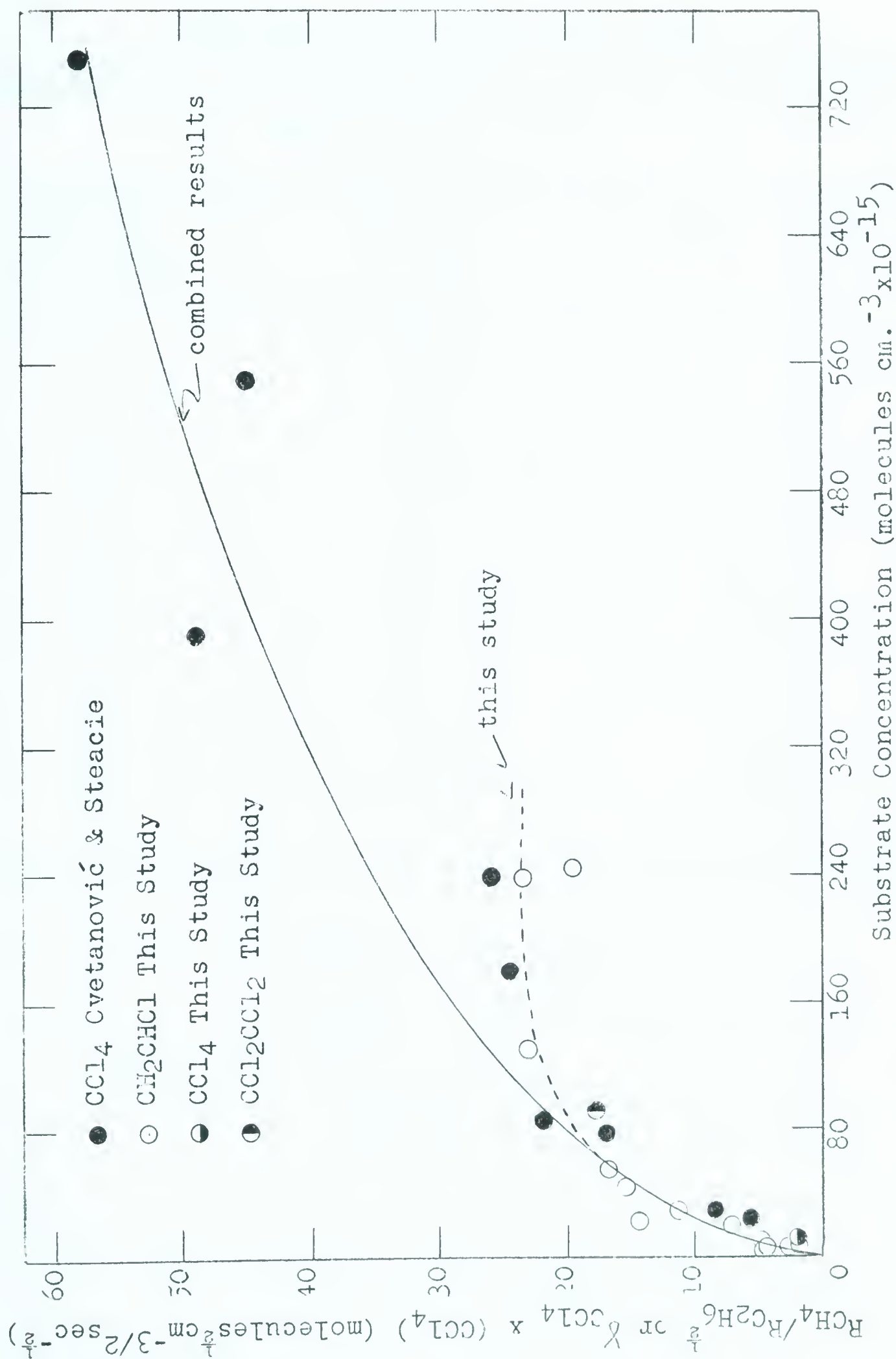


Fig. 10 $R_{CH_4}/R_{C_2H_6}^{1/2}$ vs. Substrate Conc. in various $CH_3\cdot/RCl_n$ reactions.

TABLE X

Data from Cvetanovic' et al. (33)

Photolysis of Acetone in Presence of Carbon Tetrachloride.

Temperature $\sim 150^\circ\text{C}$

$[\text{CCl}_4]$ molecules/cc $\times 10^{-15}$	$\gamma_{\text{CCl}_4}^*$ $\times 10^{11}$	$\gamma_{\text{CCl}_4} \times [\text{CCl}_4]$ $\times 10^{-6}$
23	25.2	5.8
30	28.3	8.5
78	22.0	17.2
86	26.6	22.9
180	13.7	24.7
240	10.9	26.2
390	12.6	49.1
550	8.2	45.1
750	7.7	57.8

*

$$\gamma_{\text{CCl}_4} = \frac{\frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}} - \frac{k_3}{k_2^{\frac{1}{2}}} [\text{Ac}]}{[\text{CCl}_4]}$$

the surface of the reaction vessel. Evidence for this is given by experiments using packed reaction vessels which are described in more detail in the next chapter and in Appendix 1. The findings pertinent to the present discussion are these: increasing the surface to volume ratio in the reactor decreases the extent of catalytic decomposition induced by chlorine containing compounds. Thus for a surface to volume ratio of 16 cm^{-1} (reaction vessel fully packed) the catalysis is completely suppressed. Suppression was obtained with either lime glass, pyrex or quartz Rashig rings. The similarity of the HCl concentrations resulting from the various compounds used in experiments in this laboratory and by Cvetanović¹ should be the result of the similar surface to volume ratio present in the unpacked reaction vessels (0.8 cm^{-1} in the case of the present investigation while a 120 cc. photolysis cell of the type described by Cvetanović¹ would be about 1.1 cm^{-1}).

According to such an interpretation the rate controlling steps become the adsorption and desorption of HCl from the surface.

Turning specifically to reaction (4) involving vinyl chloride a plausible mechanism is given by the sequence



Thus one should expect to observe the formation of propylene in the reaction. Two tests were made in this direction. The rate of propylene formation was compared with the estimated HCl concentration and vinyl chloride- d_3 was used in order to check whether the expected propylene- d_3 is formed. The results of these experiments are described below.

Detection of Propylene Among Reaction Products.

It was found that the ethane peak on the $\beta\beta$ -oxydipropionitrile column when trapped in liquid nitrogen and rerun on an alumina column contained small amounts of propylene. To avoid the losses inherent in the processes of trapping and rerunning, in one run, where the concentration of vinyl chloride was 267×10^{15} molecules/cc., the reacted mixture was run directly through the alumina column and only the ethane and propylene were measured. From this it was calculated that the rate of ethane formation was 13.0×10^{12} molecules/cc. sec. and 1.25×10^{15} molecules/cc. of propylene was produced in 300 sec. at 158.5°C . While the rate of ethane production seems abnormally low for this run (about half what is usually produced) the propylene produced is of the same order as the estimated HCl concentration. In a later run, again using the unpacked reactor, propylene was quantitatively measured using a 4.5% Ucon 75-H-1400, 25.2% Octoil-S on Columapak column and in this case where the concentration of vinyl chloride was 602×10^{15} molecules/cc., 13.0×10^{15} molecules/cc. of propylene was produced after 300 sec. reaction at 158.5°C as compared with the estimated steady state concentration of HCl of approximately 5×10^{15} molecules/cc..

A further run using vinyl chloride- d_3 (shown mass-spectroscopically to be of greater than 98% purity) was performed where the concentration of vinyl chloride- d_3 was 409×10^{15} molecules/cc. After 300 sec. reaction time at 158.5°C , 8.27×10^{15} molecules/cc. of propylene was produced. An analysis of the propylene by means

of the mass spectrometer showed that almost exactly half of it was propylene-d₃.

The results referred to above while not very exact quantitatively do confirm the suppositions:

- (a) Propylene is produced by the attack of methyl radicals on vinyl chloride.
- (b) The amount of propylene produced is of the same order as the amount of HCl estimated to be present at the end of the reaction.

The run with deuterated vinyl chloride shows that other means of formation of propylene are present which are still obscure, but some at least comes from the vinyl chloride.* A more detailed quantitative study of this phenomenon was considered to be unwarranted for several reasons. Until a more accurate method of determining HCl present in the system is devised the equating of this with the propylene produced would be an order of magnitude calculation only. Both HCl and propylene can react with methyl radicals and possibly with other species present in the system, and so the final concentration of these compounds is not an accurate measure of the quantities produced. The effect of the glass surface on the HCl concentration complicates matters even more.

Reactions (8) and (9) in Proposed Mechanism.

Both HCl and chlorine atoms are very reactive species and it

* It will be remembered that propylene was produced in the methyl radical/ethylene reaction which could not be explained by the proposed reaction mechanism. No propylene was detected in the decomposition of the pure DTBP.

seems very likely that they can undergo reactions other than those required specifically by the proposed reaction mechanism. HCl is difficult to measure quantitatively in a glass system and this is probably due to adsorption on the walls or, considering the alkaline nature of most glasses, by actual reaction with the glass.*

Chlorine atoms may add to double bonds as well as abstracting hydrogen and also may disappear by surface reactions. It appeared that the only way to get an insight into the importance of reactions (8) and (9) was to increase the surface to volume ratio of the reactor and see if any alteration in the product distribution takes place. This, together with the suspicion that reaction (4) may occur on the surface, led to the construction of packed reactor #1.

The Methyl Radical/Vinyl Chloride Reaction in Packed Reactors.

In order that a fuller investigation of reactions (4), (8) and (9) might be made packed reactor #1 was constructed. This was a pyrex vessel filled with lime glass Rashig rings and heated by means of an oil bath as has already been described in detail in the experimental section.

When runs are carried out in this reactor there is a dramatic change in the product distribution as shown by runs 24, 25 and 26 in Table IX, page 53. It can be seen that even at high concentrations of added vinyl chloride the rate of methane production does not increase beyond the small value which is present in the decom-

* See Appendix 1, page 79.

position of the pure peroxide and is attributable to the abstraction of hydrogen from the peroxide by methyl radicals. Isobutylene oxide has become such a minor product that it is barely detectable on the gas chromatogram and the rate of acetone production appears to be constant independent of vinyl chloride concentration. The rate of ethane production still decreases however with increase in vinyl chloride concentration.

It appears that all the reactions which depend on the presence of chlorine atoms or HCl have halted. Experiments described in Appendix 1 strongly suggest that the inhibitory effect is due to the rapid adsorption of HCl by the glass packing.

Measurement of the Rate of Addition of Methyl Radicals to Vinyl Chloride.

When the reaction is carried out in the packed reactor, the undesirable HCl catalyzed decomposition of the DTBP is suppressed and the addition reaction may be studied. Therefore a series of experiments were conducted in the packed reactor #2 to accomplish this. (Table XI, page 66).

In the presence of vinyl chloride the following polymerization reactions may be expected to occur.



etc.

Chain termination should proceed by the recombination reactions



TABLE XI

Rates of Product Formation in Methyl Radical/Vinyl Chloride Reaction in Packed Reactor #2.

Run No.	Temp. °C	Vinyl Chloride Concn. (a)			Residual Peroxide Concn. (a)	R _{CH₄} (b)	R _{C₂H₆} (b)	R _{acetone} (b)	R _{Ac} - (R _{CH₄} + 2R _{C₂H₆}) / R _{C₂H₆} ^{1/2} (c)		
		Initial Final Average							Uncorrected	f	Corrected
56	122	0	0	0	192	2.42	14.0	38.2	-		
57	122	0	0	0	189	3.32	16.2	36.1	-		
58	122	0	0	0	214	3.20	19.6	41.4	-		
60	122	26.1	28.9	27.5	206	2.59	14.0	38.0	6.26	0.55	3.44
61	122	87.8	69.9	78.9	213	2.02	9.23	36.1	16.2	0.63	10.2
64	122	131	111	121	229	2.54	7.42	38.4	24.4	0.67	16.4
65	122	161	164	163	187	3.12	4.42	34.5	34.0	0.72	24.5
66	122	161	154	158	187	1.83	4.11	30.6	32.0	0.72	23.0
63	122	164	144	154	193	2.02	4.99	33.0	29.8	0.71	21.2
62	122	252	217	235	217	1.94	3.54	39.5	51.3	0.76	39.0
52	139.5	0	0	0	173	24.3	96.5	211	-		
53	139.5	0	0	0	143	13.3	97.5	206	-		
55	139.5	13.8	11.6	12.7	197	12.3	92.0	204	2.63	0.52	1.37
54	139.5	57.9	51.4	54.7	200	13.8	65.6	211	25.8	0.58	15.0
51	139.5	140	128	134	230	13.3	55.9	236	47.0	0.65	30.6

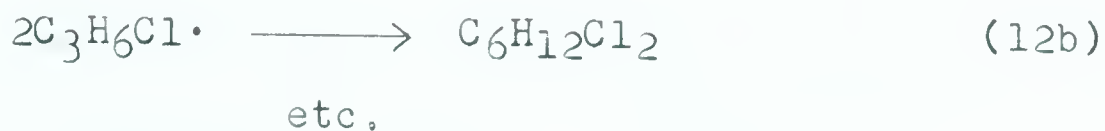
TABLE XI - Continued

50	139.5	176	199	188	222	16.6	41.2	240	69.5	0.68	47.3
49	139.5	221	223	222	236	14.2	36.6	256	95.9	0.71	68.0
48	139.5	301	269	285	219	12.0	31.9	254	99.8	0.73	72.8
67	158.5	0	0	0	195	74.3	652	1620	-		
68	158.5	0	0	0	182	68.2	753	1560	-		
69	158.5	0	0	0	186	69.7	717	1550	-		
72	158.5	97.2	87.1	92.2	195	107	533	1640	64.4	0.58	37.3
70	158.5	159	152	156	200	110	514	1730	82.3	0.62	51.0
71	158.5	183	164	174	188	122	438	1760	115	0.63	72.5
40	158.5	212	199	206	189	92	376	1480	119	0.65	77.4
74	158.5	247	224	236	170	141	314	1520	134	0.67	89.8
73	158.5	230	326	278	204	142	363	1760	146	0.68	99.3
38	158.5	354	406	380	163	87	426	2490	237	0.70	166

(a) molecules $\text{cm}^{-3} \times 10^{-15}$

(b) molecules $\text{cm}^{-3} \text{sec}^{-1} \times 10^{-11}$

(c) molecules $\text{cm}^{-3} \text{sec}^{-\frac{1}{2}} \times 10^5$



If R_{11a} is to be determined through product analysis two principal methods can be used. The first one is based on tracing the fate of the radical product of the methyl addition reaction (11a) through analysis of the products containing this radical. For this method to be analytically practicable it is necessary to suppress further polymerization (11b, 11c, etc.) by terminating the chains as in reactions (12a) and (12b). This was the method used by Brinton with ethylene and its success depends on using high enough methyl radical concentrations. It had been hoped that it could be applied also in the vinyl chloride system. It was soon found that for similar concentration conditions the chain could not be terminated after the initial addition. By carefully measuring the amount of vinyl chloride used up in typical runs (see appendix 2) it could be established that 1.4 molecules of vinyl chloride were used up per methyl radical. This leads to trichlorooctane as an expected average final product. Since the analytical difficulties in the quantitative detection of such high molecular weight products are very great and the methyl radical concentration could not be increased sufficiently, the second method for determining the rate of addition had to be used. This method is based on a material balance of the methyl radicals. In the absence of vinyl chloride



The rate of methyl radicals disappearing through addition and

termination when vinyl chloride is present, R_X is given by

$$R_X = R_{CH_3COCH_3} - R_{CH_4} - 2R_{C_2H_6}$$

Of course $R_X = R_{11a}$ only if termination always involves the recombination of two polymerizing radicals. If termination is produced always by one polymerizing and one methyl radical $\frac{1}{2}R_X = R_{11a}$. The actual factor, f , before R_X would vary from 0.5 to 1 from run to run depending on the concentration of vinyl chloride and methyl radicals. Assuming that $f = \frac{1}{2}$ * the rate data for three different temperatures have been obtained from Fig. 11 (page 70) where $R_X/R_{C_2H_6}^{\frac{1}{2}}$ is plotted against vinyl chloride concentration and the rate constant ratio $k_{11a}/k_3^{\frac{1}{2}}$ obtained from the slope. In Fig. 13 (page 71) the Arrhenius plot derived from these results is given which leads to the rate equation

$$\frac{k_{11a}}{k_3^{\frac{1}{2}}} = 2.5 \times 10^{-5} e^{-9730/RT} \text{ cm}^3 \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$$

Before discussing this result a corrective procedure should be mentioned which estimates the values of f under varying experimental conditions. Details of the method are given in Appendix 3. It suffices to say here that the procedure takes into account variation of the vinyl chloride and methyl radical concentrations and is based on a comparison with the ethylene system where the information is much more complete. The computed values of f are given in the second last column of Table XI (page 66) and the corrected rate constant ratio in the last column. The corrected rate plots are shown in Figs. 13 and 14 (pages 72 and 73).

* See approximate evaluation of f in Appendix 3.

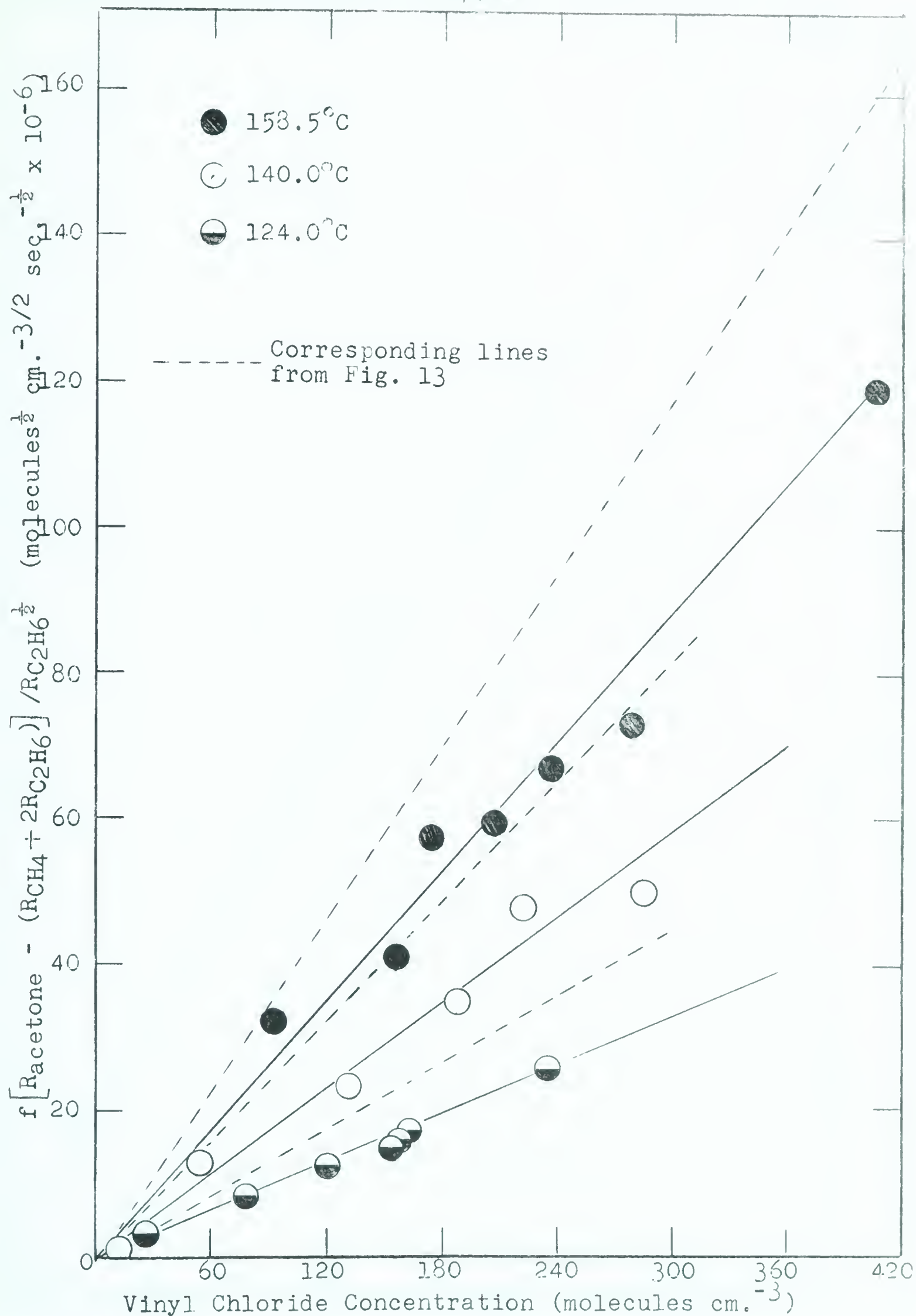


Fig. 11 Kinetic plot of data in methyl radical/vinyl chloride reaction. $f = \frac{1}{2}$

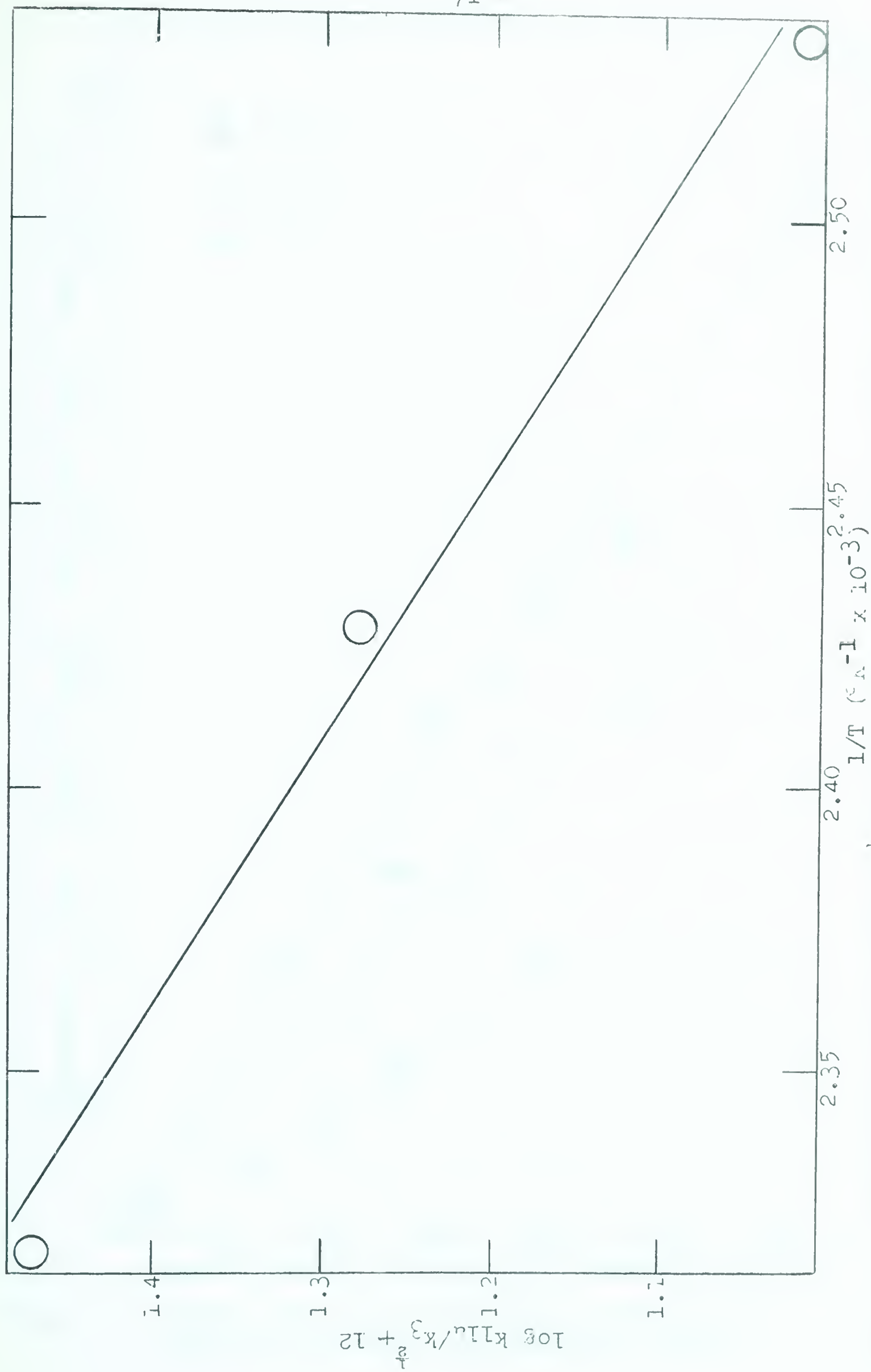


Fig. 12 Arrhenius plot for $k_{11a}/k_3^{\frac{1}{2}}$ in $\text{CH}_3\cdot/\text{C}_2\text{H}_3\text{Cl}$ reaction. $f = \frac{1}{2}$

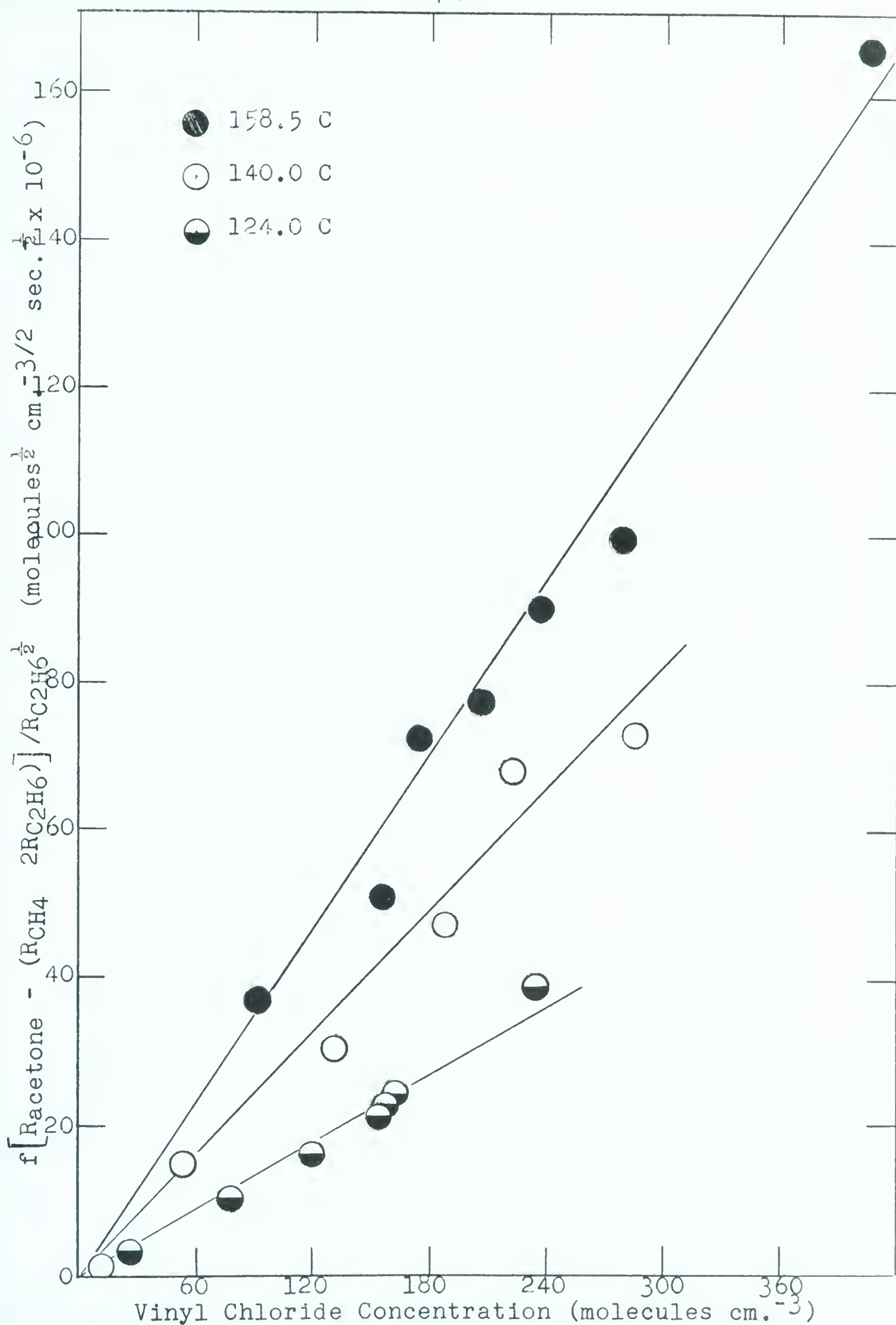


Fig. 13 Kinetic plot of data in methyl radical/vinyl chloride reaction. f = calculated value.

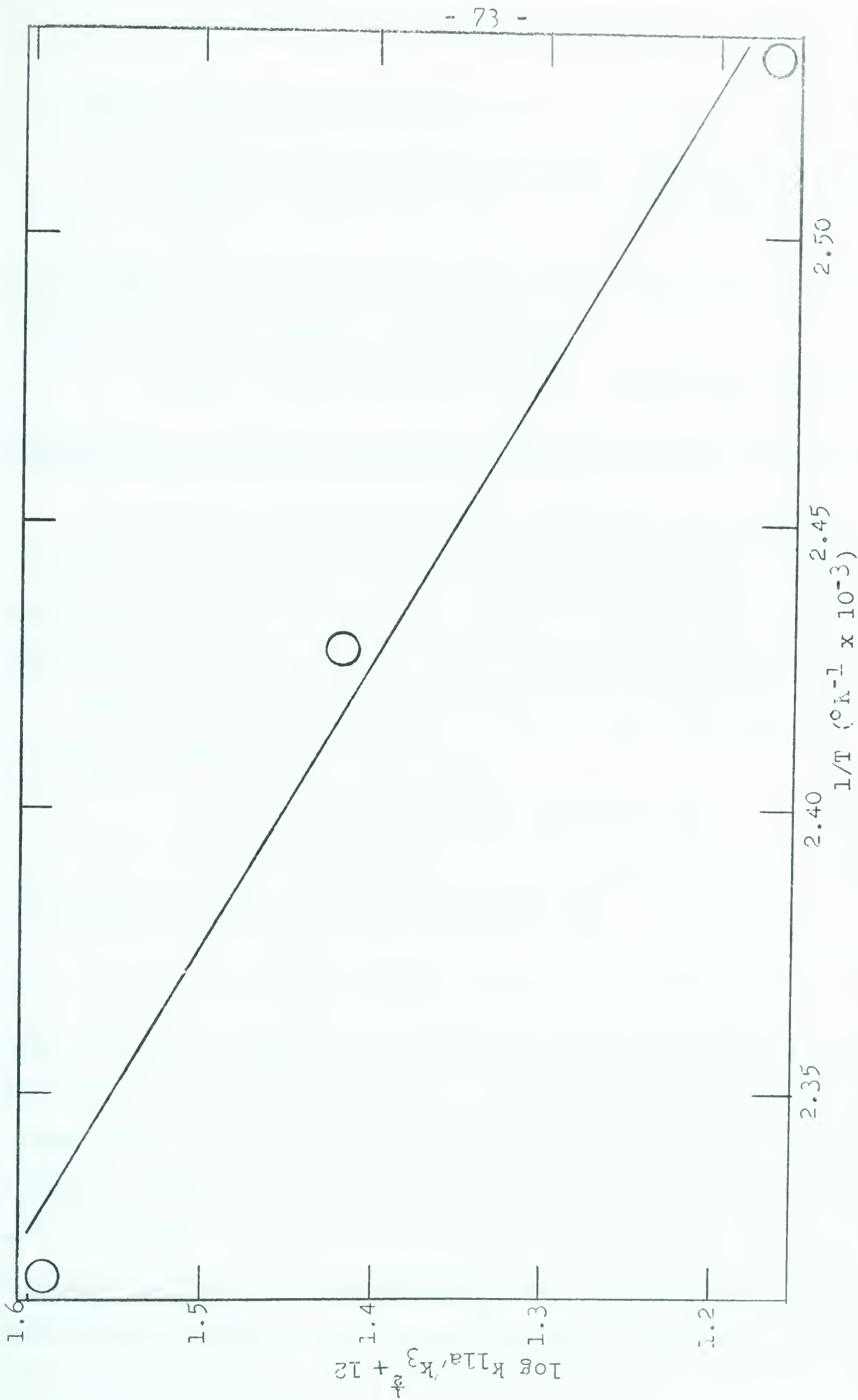


Fig. 14 Arrhenius plot for $k_{11a}/k_3^{1/2}$ in $\text{CH}_3\cdot/\text{C}_2\text{H}_3\text{Cl}$ reaction. $f =$ calculated value.

The corrected rate equation is

$$\frac{k_{11a}}{k_3^{\frac{1}{2}}} = 1.53 \times 10^{-6} e^{-9053/RT} \text{ cm}^{\frac{3}{2}} \text{ molecule}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$$

Using Gomer and Kistiakowsky's (10) value of $k_3 = 7.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $E_3 = 0$ we obtain

$$k_{11a} = 1.3 \times 10^{-11} e^{-9053/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Significance of Result on Methyl Addition to Vinyl Chloride.

Comparing the individual rate constants with Brinton's values for ethylene one finds that in the temperature range 120-160°C the addition of methyl to vinyl chloride is roughly three times faster. Thus the chlorine substituent has a considerable activating effect.

Szwarc (6) in unpublished work has found that in isoocatne solution at 65°C $k_2/k_1 = 960$ where



For ethylene under the same conditions (1)

$$\frac{k_2}{k_1} = 34$$

Thus the rate of addition of methyl to vinyl chloride is about 28 times as fast as to ethylene. Extrapolation of the data reported here and that of Brinton's on ethylene to 65°C results in a rate of addition to methyl to vinyl chloride 3.5 times faster as to ethylene at this temperature. The conditions are very different and so no close agreement can be expected, however the discrepancy is bigger than the experimental differences should

warrant.

In other work Szwarc has found that under these same conditions (isooctane solution at 65°C) chloroprene adds methyl radicals 3.5 times faster than butadiene and isoprene (5) and 2-chlorobenzoquinone 1.5 times faster than benzoquinone (39). A similar activating effect of chlorine substitution has been observed in co-polymerization studies where the reactivity was found to increase 3-30 times (40).

Burnett and Wright (20) (see introduction) found values for k_p , the rate constant for propagation in the polymerization of vinyl chloride in tetrahydrofuran, at two temperatures, 25°C and 55°C, and from this obtained an Arrhenius expression for the rate constant. Comparing these values with those found by extrapolation from the data obtained in this study we find:

	$k_{25^\circ\text{C}}$	$k_{55^\circ\text{C}}$	A^*	E^{**}
Burnett and Wright	6.2×10^3	11×10^3	5.5×10^{-15}	3.700
This Study	2×10^3	8×10^3	1.53×10^{-11}	9.053

While the rates are comparable at the temperatures quoted the values determined for the Arrhenius parameters are in very poor agreement. Close agreement between such greatly differing systems could not be expected, however Burnett and Wright's data do not agree well with those from other similar polymerization systems (40) and in particular their activation energy is probably considerably too low.

While it would be of interest to determine whether the activating effect of chlorine atoms is exerted through the pre-exponential factor or the activation energy, the data is not suf-

* $\text{cm}^3\text{molecule}^{-1}\text{sec}^{-1}$

** k.cal. mole^{-1}

ficiently accurate to do this (an error of 5% in the rate constants for the two extreme temperatures bring about a 1 kcal error in the activation energy) although Szwarc (18) in suggesting an explanation for this effect concludes that it is, in fact, the activation energy. (See Introduction.)

If we examine Szwarc's explanation we see that, in his opinion, the methyl radical behaves rather like a nucleophilic reagent. Thus in styrene the electron withdrawing phenyl group causes an increase in reactivity over that of ethylene (Table I). In propylene the electron donating methyl group should lead to a decrease in reactivity when compared with ethylene and Szwarc's results indicate that this is the case. However if, as James and Steacie (3) think, the value for ethylene should be divided by 2 to allow for the fact that it has two C atoms on which addition may take place as compared to α substituted ethylenes, then propylene is more reactive than should be expected.*

An alternative to Szwarc's explanation is to assume that if conjugation lowers the energy of the initial addition product this will make the attractive curve in Fig. 1a (page 16) lower where it crosses the repulsive curve Fig. 1c (page 16) so reducing the activation energy. Methyl substituents would effect this through hyperconjugation and phenyl groups and hetero atoms like chlorine would also give resonance stabilization. In both explanations we can expect that substitution of both ends of the bond

* Miyoshi and Brinton (16) found that ethylene and propylene add methyl at approximately the same rate as also did Baal and Danby (44) but Beek and Rust (45) and Eltenton (46) found that propylene reacts faster. Thus Szwarc's results must be treated with caution.

will reduce the rate of addition due to steric hindrance.

Attempts have been made, all with some success, to correlate the rate of radical addition with free valence (41), atom localization energy (42) and even heat of reaction (43). The lack of unequivocal data on addition reactions and the uncertainty in calculating some of these quantities has prevented any final conclusion from being reached.

Suggestions for Further Study.

Several topics for further research are indicated by this work, the most intriguing being an investigation of the exact nature of reaction (4), the liberation of a chlorine atom from a chlorinated compound by methyl radical attack. Perhaps the thermal decomposition of DTBP in the presence of carbon tetrachloride would be the best system for detailed study. A careful analysis of the products would probably reveal 1,1,1-trichloroethane and, if a suitable accurate means of measuring HCl concentration were devised, the investigation could be put on a quantitative basis.

The rate of addition of methyl radicals to vinyl and vinylidene fluoride and bromide would supply data needed to develop a theoretical explanation of the activating effect of a halogen atom. The fluorides are particularly promising since one might expect no complicating side reactions.

While it has been assumed that the initial methyl addition to vinyl chloride occurs on the unchlorinated carbon, this has

not been proved.* Runs at high pressures of vinyl chloride might allow one or the other of the two isomeric dichlorohexanes, which will result from the combination of chloropropyl radicals, to be detected if a suitable analytical system were available.

* Addition of CCl_3 to a variety of olefins of the type R-CH=CH_2 by Kharasch and Sage (47) showed exclusive addition to the CH_2 group. Addition of CF_3 to similar olefins including vinyl chloride by Haszeldean (48) gave identical results.

APPENDIX 1

Examination of the Adsorption of HCl on Glass.

As has been shown, when the methyl radical/vinyl chloride reaction is carried out in a packed reactor the effect on the distribution of products is compatible with HCl being removed from the reaction system as soon as it is formed. The most likely explanation for this is that the HCl is being adsorbed by the glass packing. To determine whether this does indeed occur, the apparatus shown in Fig. 15 (page 80) was constructed. It consisted of the packed reactor #1 connected to a 500 cc. pyrex bulb with breakseals attached as shown. The whole assembly was mounted on a stand and could be placed inside an oven maintained at about 160°C.

The method of operation was as follows:

Breakseal A was filled with HCl to a known pressure and attached to the assembly. The assembly was heated to 160°C in the oven and evacuated and sealed by heating constriction #1 while still hot. (This should remove any reversibly adsorbed surface layer on the glass.) The HCl was now allowed to flow through the apparatus by breaking breakseal A, and the assembly was put back in the oven for about 10 minutes. It was now removed again and constriction #2 sealed. When the apparatus was cool, 2 cc. of distilled water was placed in breakseal B, the sidearm sealed and the breakseal broken.

After standing for some time so that any HCl still present in the 500 cc. bulb could dissolve in the water, the breakseal

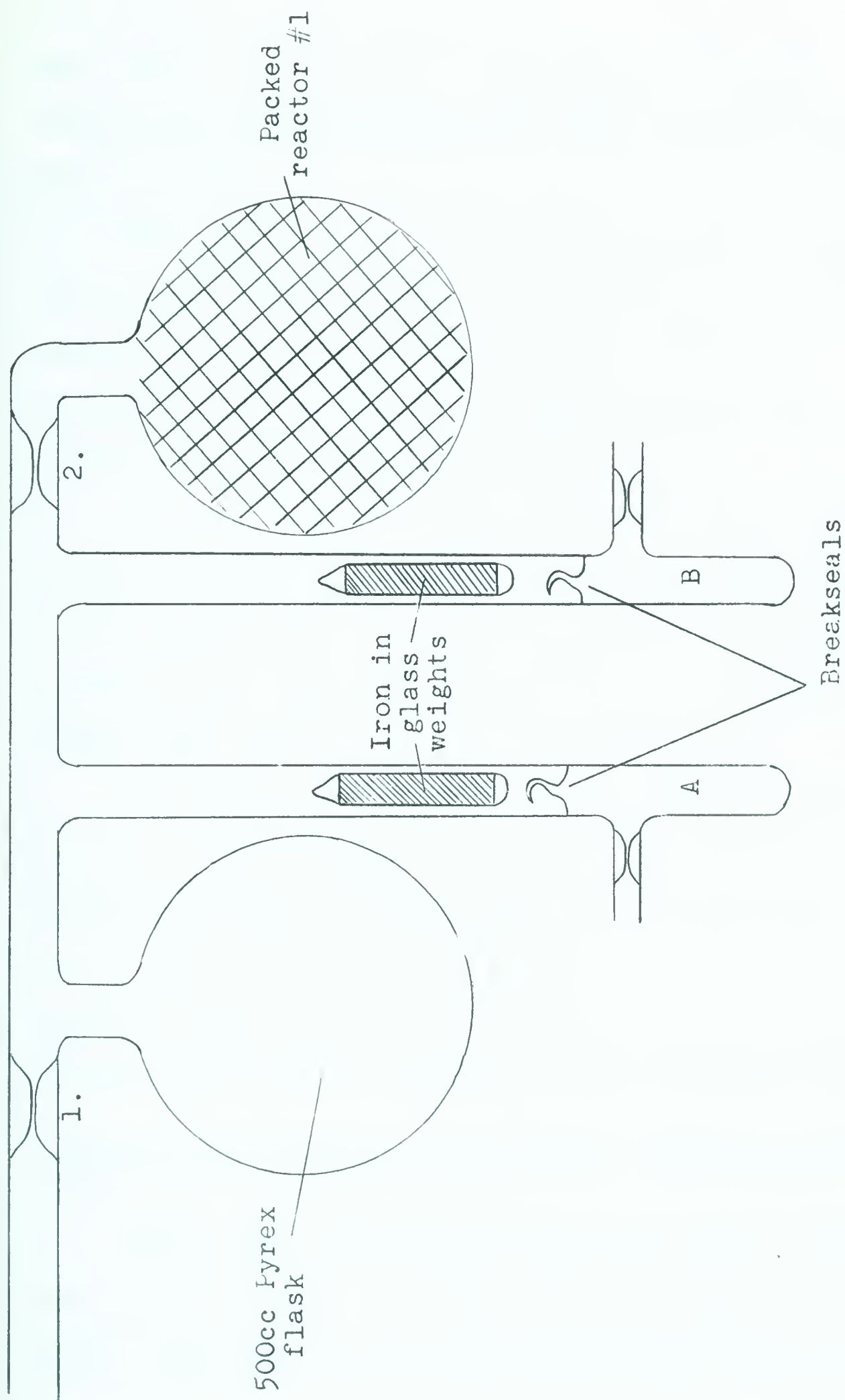


Fig. 15 Apparatus used in study of HCl adsorption.

was cut out and the pH of the water determined. Results of a series of investigations with this apparatus are shown in Table XII, page 82).

The results show that when pressures of HCl much greater than that possibly present during the reaction are used in the apparatus, all the HCl is removed. Rinsings of the packed and unpacked bulbs are slightly alkaline indicating that the HCl is irreversibly adsorbed on the glass.

Before the last run was performed the packed bulb was rinsed with about 20 cc. of concentrated hydrochloric acid for a few minutes and then put in the oven overnight to drive off the excess acid. Again the results of the adsorption experiment shows that the packing will remove HCl gas.

It appears therefore that HCl does react with the glass but either a certain amount of the HCl is reversibly adsorbed on the surface and can be driven off again by heating* or the reaction of the HCl with the glass depends on a slow penetration of the acid to deep lying active sites and so the effect of the surface cannot be destroyed without a very prolonged treatment with acid.

Experimental Studies on the Rate of Adsorption of HCl on Glass.

While these experiments show that HCl is adsorbed, or perhaps more accurately, chemisorbed, on lime glass they give no clear indication as to the rate at which this sorption takes place.

* while it is possible that the adsorbed HCl can be removed by heating but not by washing with water (as shown by the alkaline nature of the rinsings of the packed bulb after the experiment) this alternative is the less plausible.

TABLE XII

Results of Experiments in HCl Adsorption Apparatus.

Volume of breakseal (cc)	Pressure of HCl in breakseal (mm)	pH of distilled water	pH of 2 cc. solution	pH of rinsings of packed bulb	pH of rinsings of unpacked bulb
8.33	3.74	6.7	6.7		
7.85	12.9	6.7	4.3		
7.33	27.4	6.4	7.4		
8.16	64.6	5.7	6.1		8.4
<u>Packed Bulb Treated With Concentrated HCl.</u>					
7.11	109.8	6.3	5.9	8.1	7.3

Dimensions of Adsorption Apparatus.

Volume of packed bulb	326 cc.
Volume of unpacked bulb	500 cc.
Volume of connecting tubing	15 cc.
Total volume of apparatus	840 cc.
Surface area of packed bulb	4920 sq. cm.
Surface area of unpacked bulb	532 sq. cm.
Surface area of connecting tubing	220 sq. cm.
Total surface area of apparatus	5672 sq. cm.

Obviously if the sorption is to be an adequate explanation for the alteration in reaction products when the methyl radical/vinyl chloride reaction is carried out in a packed reactor it must be sufficiently rapid for the HCl to be sorbed as quickly as it is formed.

To get an approximate measure of this rate of sorption, an Octoil-S manometer was connected to the capillary tube which formed the inlet to the packed reactor #2. HCl was allowed to enter the reactor and the two-way stopcock (SC1 in Fig. 1, page 16) closed. The pressure was read on the manometer and the reading repeated every 30 seconds. Several experiments of this type were performed and typical results are shown in Table XIII (page 84) and Fig. 16 (page 85).

There are several drawbacks to this simple experimental system: (a) Very rapid sorption occurring within less than about 1 minute will not be detected because the response of the manometer is very sluggish.

(b) After the manometer has been initially depressed by the pressure of HCl, Octoil-S clings to the walls and takes an appreciable time to flow back to join the bulk of the manometric fluid. This gives the appearance of an initial fairly rapid adsorption.

(c) If the experiment is continued for a considerable time, fluctuations in the ambient temperature will cause scatter in the results due to change in density of the manometric fluid.

(d) Experiments must necessarily be conducted with higher pressures of HCl than those calculated to be present in the methyl

TABLE XIII

Kinetic Data on HCl Adsorption on Lime Glass in Packed Reactor #2
During Initial 15 minutes.

HCl Adsorption			Air Control (a)		Air Control (b)	
Height of manometer at zero pressure = 55.43 cm.			= 53.15 cm.		= 53.25 cm.	
Time (mins.)	Manometer Height (cm.)	Manometer Height (corrected) (cm.)	Time (mins.)	Manometer Height (cm.)	Time (mins.)	Manometer Height (cm.)
0	31.07	31.63	0	33.01	0	27.95
$0\frac{1}{2}$	31.44	31.81	$0\frac{1}{2}$	33.14	$0\frac{1}{2}$	28.20
1	31.68	31.97	1	33.20	1	28.31
$1\frac{1}{2}$	31.85	32.09	$1\frac{1}{2}$	33.25	$1\frac{1}{2}$	28.35
2	31.97	32.18	2	33.27	2	28.39
$2\frac{1}{2}$	32.12	32.31	$2\frac{1}{2}$	33.29	$2\frac{1}{2}$	28.41
3	32.22	32.39	3	33.31	3	28.42
$3\frac{1}{2}$	32.32	32.47	$3\frac{1}{2}$	33.33	$3\frac{1}{2}$	28.43
4	32.44	32.57	4	33.35	4	28.47
$4\frac{1}{2}$	32.51	32.63	$4\frac{1}{2}$	33.36	$4\frac{1}{2}$	28.48
5	32.59	32.70	5	33.37	5	28.50
$5\frac{1}{2}$	32.65	32.74	$5\frac{1}{2}$	33.39	$5\frac{1}{2}$	28.51
6	32.72	32.79	6	33.41	6	28.53
$6\frac{1}{2}$	32.79	32.86	$6\frac{1}{2}$	33.42	$6\frac{1}{2}$	28.53
7	32.84	32.90	7	33.43	7	28.54
$7\frac{1}{2}$	32.91	32.96	$7\frac{1}{2}$	33.44	$7\frac{1}{2}$	28.55
8	32.95	32.99	8	33.45	8	28.55
$8\frac{1}{2}$	33.00	33.03	$8\frac{1}{2}$	33.47	$8\frac{1}{2}$	28.55
9	33.04	33.07	9	33.48	9	28.55
$9\frac{1}{2}$	33.08	33.10	$9\frac{1}{2}$	33.50	$9\frac{1}{2}$	28.55
10	33.12	33.14	10	33.50		
$10\frac{1}{2}$	33.17	33.18	$10\frac{1}{2}$	33.51		
11	33.21	33.22	11	33.52		
$11\frac{1}{2}$	33.26	33.26	$11\frac{1}{2}$	33.53		
12	33.29	33.29	12	33.53		
$12\frac{1}{2}$	33.33	33.33	$12\frac{1}{2}$	33.53		
13	33.37	33.37	13	33.53		
$13\frac{1}{2}$	33.41	33.41	$13\frac{1}{2}$	33.53		
14	33.45	33.45	14	33.53		
$14\frac{1}{2}$	33.49	33.49				
15	33.53	33.53				

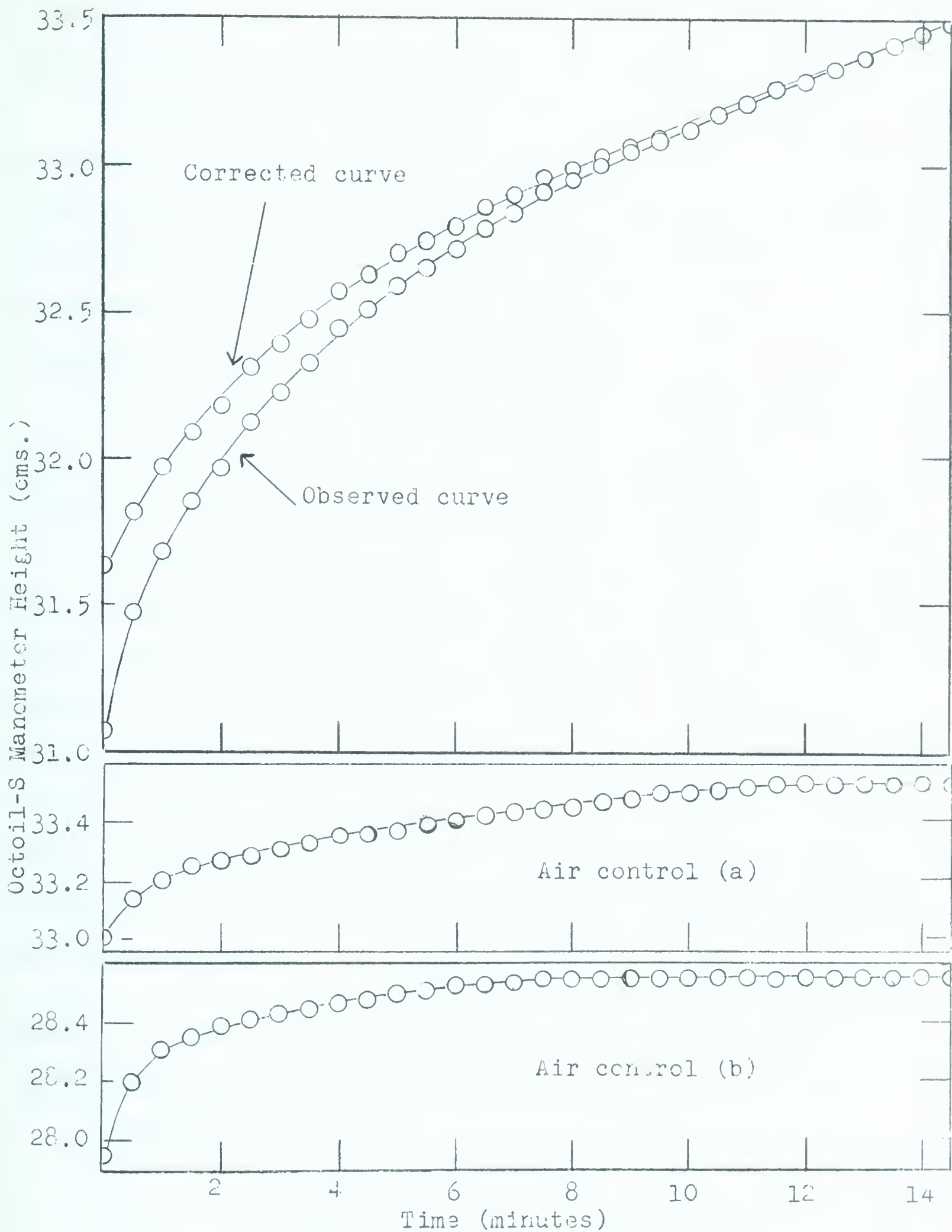


Fig. 16 HCl adsorption on lime glass in packed reactor #2 during initial 15 minutes.

radical/vinyl chloride reaction in order that a simple manometer may be used to measure the changes in pressure.

The difficulty (b) can be corrected for by introducing air in blank experiments and finding the effect introduced by the slow response of the manometer. Plots of two such experiments are shown along side one using HCl in Fig. 16 (page 85) and a corrected curve calculated from the average of the runs with air combined with the HCl data is also shown.

The main feature of the P/t plots for $t < 15$ minutes is an initial rapid rise (which is not solely attributable to the time lag in the manometer response) followed by a linear portion.

Although it has no direct bearing on the main investigation, in one experiment the measurement of the pressure change with time was continued for 17,000 minutes and the results (Table XIV, page 87) are plotted in Fig. 17 (page 88). A logarithmic time scale is used and the plot appears to consist of several linear portions of different gradient divided by transitional curves.

This behaviour is quite common in various systems of gaseous chemisorption on solids and can be described in terms of Elovich's

empirical equation
$$\frac{dq}{dt} = ae^{-\alpha q} \quad (1)$$

where q is the amount chemisorbed at time t and a and α are constants during any one experiment.

Assuming $q = 0$ at $t=0$

$$q = \frac{2.3}{\alpha} \log(1 + a\alpha t) \quad (2)$$

or
$$q = \frac{2.3}{\alpha} \log(t+t_0) - \frac{2.3}{\alpha} \log t_0 \quad (3)$$

$$\text{where } t_0 = \frac{1}{a\alpha}$$

TABLE XIV

Kinetic Data on HCl Adsorption on Lime Glass in Packed Reactor #2
Over a Prolonged Period.

Time (mins.)	Manometer Height (cms.)	Time (mins.)	Manometer Height (cms.)	Time (mins.)	Manometer Height (cms.)
0	12.64	14½	15.33	665	25.73
½	14.32	15	15.35	699	26.37
1	14.46	15½	15.36	719	26.76
1½	14.61	16	15.38	1414	33.13
2	14.71	16½	15.39	1437	33.25
2½	14.79	17	15.41	1460	33.33
3	14.87	17½	15.42	1491	33.45
3½	14.90	18	15.42	1556	33.67
4	14.96	18½	15.42	1606	33.92
4½	15.00	19	15.42	1685	34.39
5	15.02	19½	15.42	1753	34.51
5½	15.05	27	15.61	1784	34.66
6	15.06	59	16.07	1853	34.83
6½	15.07	76	16.31	1923	34.97
7	15.08	106	16.62	2807	36.98
7½	15.09	174	17.70	3739	38.91
8	15.10	193	17.90	4597	40.05
8½	15.11	223	18.20	4978	40.51
9	15.13	250	18.43	5679	41.24
9½	15.14	277	18.88	6137	41.56
10	15.16	300	19.29	6541	41.81
10½	15.17	316	19.60	7149	42.51
11	15.19	353	20.34	8590	43.12
11½	15.20	392	21.02	10060	43.51
12	15.22	454	22.09	11479	43.47
12½	15.25	543	23.70	11659	43.86
13	15.27	575	24.12	12967	44.11
13½	15.29	606	24.62	14638	43.84
14	15.30	637	25.18	16124	44.53
				16791	44.43

Height of Manometer at zero pressure = 53.44 cm. Octoil-S.

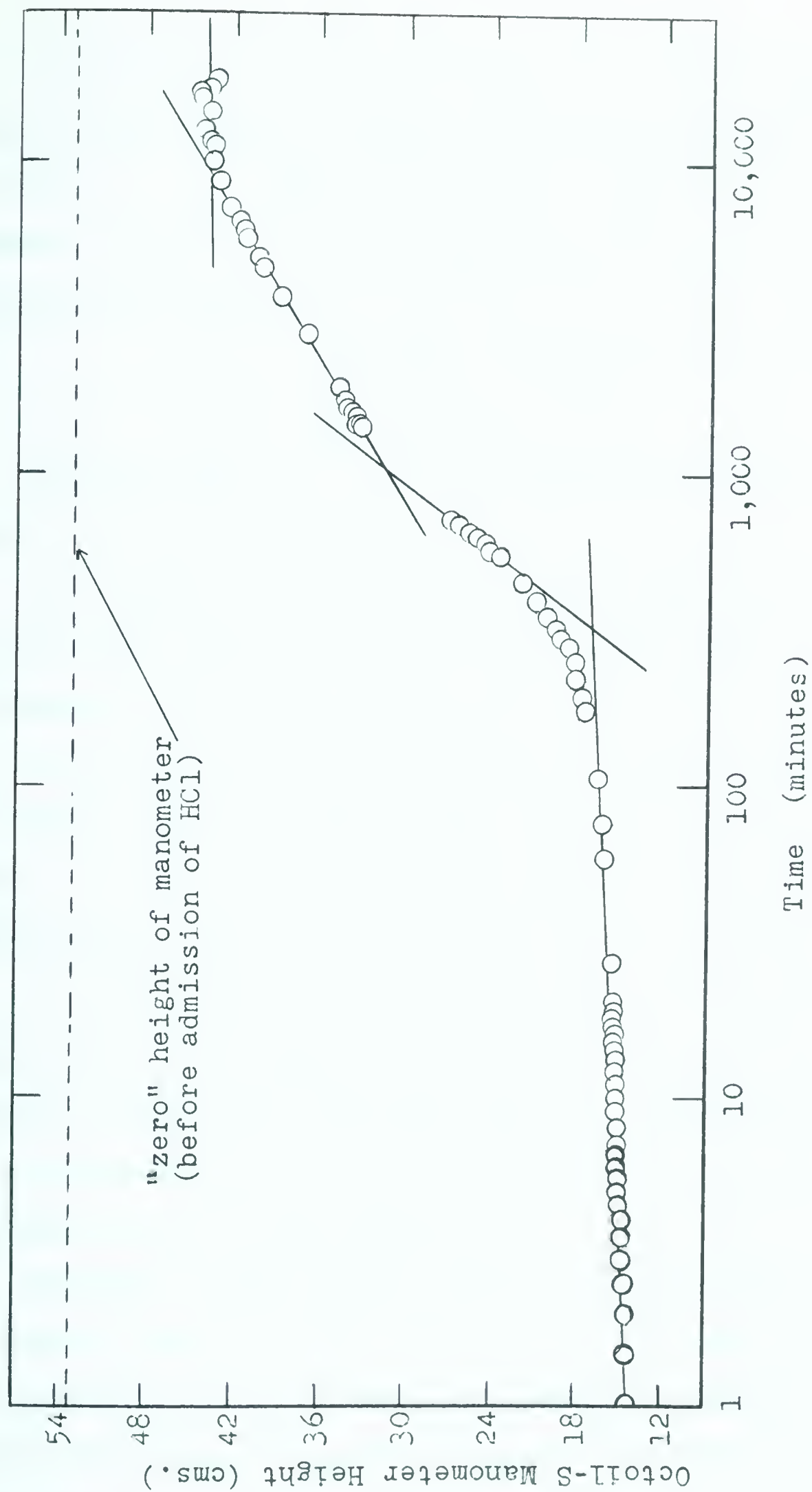


Fig. 17 HCl adsorption on lime glass in packed reactor #2 over extended period. ("Elovitch" plot).

If a volume of gas q_0 is adsorbed instantaneously and before equation (1) begins to apply, the integrated form of the equation becomes

$$q = \frac{2.3}{\alpha} \log (t+k) - \frac{2.3}{\alpha} \log t_0 \quad (4)$$

where $k = t_0 e^{q_0}$. If k is negligible in comparison with t , then equation (4) reduces to

$$q = \frac{2.3}{\alpha} \log t - \frac{2.3}{\alpha} \log t_0 \quad (5)$$

or

$$q = \frac{2.3}{\alpha} \log a \propto t \quad (6)$$

Thus an "Elovitch" plot of amount adsorbed versus $\log t$ should be a straight line.

The several linear portions of the plot are considered to be different kinetic stages of the chemisorption each with characteristic values of a and α .

A full discussion of the application of the Elovich equation to various chemisorption systems can be found in a review article by M. J. D. Low (49) but no data on the HCl/glass system is presented there nor can it be found in the literature.

An unfortunate feature of the study of chemisorption to-date is the lack of agreement in experimental results between different research groups and the wide variety of interpretations which have been advanced, all with some merit but none which adequately explain all the effects observed.

Insofar as the present results are concerned, the HCl/glass system is similar to many other gas/solid chemisorption systems, but any attempt on the basis of the results presented here to correlate it more closely with any one of the other systems would be of doubtful value.

It should be stressed, however, that Elovich plots are only

applicable to "slow" chemisorption, i.e. to chemisorption which occurs over periods greater than several minutes and is therefore amenable to experimental measurement. There is good reason to believe that "fast" chemisorption which occurs within time intervals less than about one minute is present in many systems, although no accurate quantitative studies have been made of this, and no doubt this is true of the HCl/glass system. Such fast chemisorption may be the correct explanation of the rapid removal of HCl from the gas phase by the lime glass in the packed furnaces.

Some further experiments were conducted in which the packed reactor #2 (modified by fitting to it a ground glass greaseless stopper, which utilized an "Atcoseal" high temperature silicone rubber "O" ring, so that the packing could be changed readily) in which the lime glass Rashig rings were replaced with several other types of packing. The packings used and the results obtained are as follows.

(a) When pyrex Rashig rings of similar dimensions to the original lime glass rings were used no methane or isobutylene oxide were found in significant amounts among the products.

(b) In an attempt to render the surface acidic, the pyrex packing was soaked in dilute phosphoric acid and then the reactor was heated under vacuum to remove the water. Reactions performed in the reactor gave anomalous results in that only very small quantities of DTBP could be recovered after reactions. This appeared to be due to the DTBP reacting with, or being adsorbed by, the phosphoric acid.

(c) Rashig rings, also of similar dimensions but made from quartz

tubing, were used but the results were again the same as with pyrex or lime glass.

(d) To check that the results obtained in the original unpacked reactor had not been due to some peculiarity of its surface, and therefore atypical, experiments were performed in which all the packing was removed from the modified packed reactor #2. Methane and isobutylene oxide were found to be major products and the reaction appeared identical to that in the original unpacked reactor.

The results in the pyrex and quartz packings, where the surfaces can be expected to be much less alkaline than the lime glass, seem to indicate that fast adsorption (rather than chemisorption) is sufficient to remove the HCl formed in the reaction. Unfortunately the phosphoric acid coated surface alters the reaction so much that no useful conclusions can be drawn from the experiments performed on it.

Runs with HCl in the packed reactor (Table IX, page 52) show that the catalytic effect of the HCl is not stopped (it may be reduced somewhat but the uncertainty in the measurement of the HCl concentration makes a definite conclusion unwarranted) which indicates that the surface cannot remove such large quantities very quickly - a conclusion also reached from the rate studies on HCl adsorption already mentioned. This gives further reason for supposing that in the case of lime glass, a fast physical adsorption by a limited number of surface sites followed by slower chemisorption to deep lying sites is the correct explanation.

A few experiments were performed in the adsorption apparatus shown in Fig. 15 and described on page 79 in which the lime glass

packing was replaced with pyrex. An outline of the results is given below.

Experiment Number	1	2	3	4
Amount of HCl introduced*	258	56.8	25.8	51.6
Amount of HCl recovered*	60	9.0	3.2	3.8
% of HCl recovered	24%	15.9%	12.4%	7.4%
<u>Amount of HCl in gas phase</u> <u>Amount of HCl on surface</u>	$\frac{G}{A}$ 0.25	0.06	0	---

Experiments 1-3 were conducted in the manner described previously. Experiment 4 differed in that the packed vessel was not sealed off from the rest of the apparatus before the residual HCl was allowed to dissolve in the distilled water.

According to the dimensions of the apparatus, the unpacked section which was isolated and opened to the distilled water in Experiments 1-3 represents approximately 65% of the total volume and 13% of the total surface area. Thus if there were no adsorption we would expect 65% recovery of HCl. If there were complete reversible physical adsorption we would expect 13% recovery of HCl.

The function G/A is calculated assuming that the adsorption is reversible using the equations

$$\begin{aligned} \text{HCl}_{\text{introduced}} &= G + A \\ \text{HCl}_{\text{recovered}} &= 0.65G + 0.13A \end{aligned}$$

where G = no. of molecules in gas phase

A = no. of molecules adsorbed

* (molecules $\times 10^{-17}$)

The estimated concentration of HCl present during kinetic runs in the unpacked reactor corresponds to a value approximately equal to that present in Experiment 3.

The calculated values of G/A , if correct, would readily account for the suppression of the HCl catalyzed reaction in pyrex-packed reactors. However, on the basis of the theory that the adsorption of HCl in pyrex is completely reversible, the recovery of HCl in Experiment 4 should be 100% and so considerable doubt is cast on the calculated values of G/A for the other experiments.

There are several drawbacks to the use of Experiment 4 to decide whether the adsorption of HCl on pyrex is completely reversible the greatest being that during the period (about 14 hours) during which the distilled water is exposed to the system and during which the available HCl should dissolve in it, the packed vessel dropped to room temperature where physical adsorption can be expected to be much stronger.

Reviewing these results the only conclusion which can be drawn is that pyrex adsorbs HCl but either to a lesser extent than lime glass or by means of a reversible process as opposed to the irreversible process found with lime glass. It is not clear whether the adsorption is sufficient to suppress the catalyzed reaction in a packed reactor.

An adequate investigation of the removal of HCl by the various surfaces obviously requires a more sophisticated experimental system designed for this particular purpose and capable of measuring HCl pressures in situ under experimental conditions (e.g. at

160°C in the packed reactor). A diaphragm capacitor micromanometer connected to an electrically heated reactor would be a possible solution.

APPENDIX 2

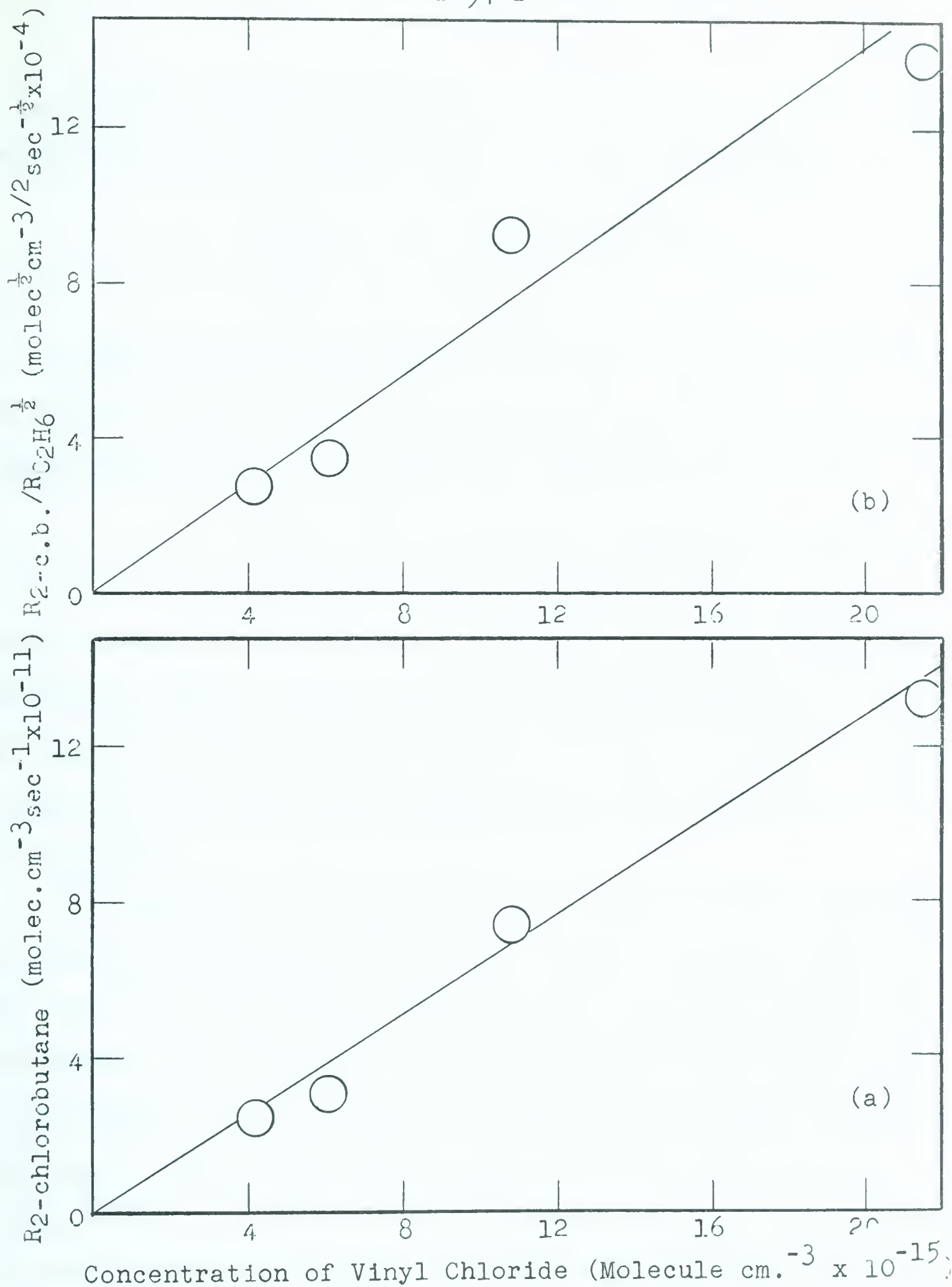
In this study of the methyl radical/vinyl chloride reaction it has been tacitly assumed that addition to the double bond does take place but no conclusion as to the distribution of the products of such a reaction have been drawn. Of the possible chlorinated hydrocarbons resulting from reactions (11), (12), (13), etc. only 2-chlorobutane was analyzed for and, because of the experimental complexity introduced by trapping out the peroxide peak on the $\beta\beta$ -oxydipropionitrile column, this was done in a few runs in the unpacked reactor. These results are shown in Table XV and the rate of 2-chlorobutane production is plotted as a function of vinyl chloride concentration in Fig. 18a, page 94. While some loss of 2-chlorobutane may be expected during the trapping and rerunning procedures, it does not appear that this product can account for all the methyl radicals which disappear through an addition reaction.

TABLE XV

Rate of 2-Chlorobutane Production in Methyl Radical/Vinyl Chloride Reaction in Unpacked Reactor.

Run No.	Average Vinyl Chloride Conc. (a)	$R_{C_2H_6}$ (b)	$R_{2\text{-chlorobutane}}$ (b)	$\frac{R_{2\text{-chlorobutane}}}{R_{C_2H_6}^{1/2}}$ (c)
3	4.16	771	2.43	2.77
4	6.05	778	3.10	3.52
7	10.83	652	7.40	9.15
8	21.5	919	13.2	13.8

(a) molecules cm^{-3} $\times 10^{-15}$
 (b) molecules $cm^{-3} sec^{-1}$ $\times 10^{-11}$
 (c) molecules $cm^{-2} sec^{-2}$ $\times 10^{-4}$



Figs. 18a, 18b Plots of R2-chlorobutane and R2-chlorobutane/
R_{C₂H₆}^{1/2} versus vinyl chloride concentration for
methyl radical/vinyl chloride reaction in
unpacked reactor.

If the 2-chlorobutane were to account for all the addition we could obtain the rate of addition from the equality

$$\frac{k_{11}}{k_3^{\frac{1}{2}}} = \frac{R_{2\text{-chlorobutane}}}{R_{C_2H_6}^{\frac{1}{2}}}$$

Using the data available for the production of 2-chlorobutane at 158.5°C we can plot $R_{2\text{-chlorobutane}}/R_{C_2H_6}^{\frac{1}{2}}$ versus vinyl chloride concentration (Fig. 18b, page 94). From this we obtain the value

$$\frac{k_{11}}{k_3^{\frac{1}{2}}_{158^\circ}} = 7.1 \times 10^{-12} \text{ molecule}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}}$$

which is about 5 times smaller than that calculated from the rate of methyl radical disappearance in the packed reactor.* It will be noted that this data was obtained at very low vinyl chloride concentrations where any polymerization would be expected to be at a minimum.

If the amount of vinyl chloride consumed in the reaction could be measured and compared with the number of methyl radicals not accounted for by methane or ethane production the average size of the chlorinated products of addition would be determined. Such a measurement from the data available would require finding the difference between two large values (initial vinyl chloride concentration and final vinyl chloride concentration) which are measured by different means (mercury manometer height and gas

* $\frac{k_{11}}{k_3^{\frac{1}{2}}_{158.5^\circ}} = 39 \times 10^{-12} \text{ molecule}^{-\frac{1}{2}} \text{ cm}^{\frac{3}{2}} \text{ sec}^{-\frac{1}{2}} \text{ (corrected)}$

chromatography peak area) and any result obtained would be very inaccurate.

To increase the accuracy of the determination a method was devised by which the amount of vinyl chloride recovered after a run was compared with the amount recovered from a blank using the same original mixture and on which the same experimental operations were performed. Details of this method and calculations from a typical run are to be found below.

In this way it was shown that 1.4 molecules of vinyl chloride are removed for every methyl radical consumed other than by methane or ethane production. Thus it can be concluded that the average product from the addition is trichlorooctane. Probably there is a spectrum of chlorinated hydrocarbon products ranging from 2-chlorobutane to about pentachloro-C₁₂ compounds, the distribution curve peaking at trichlorooctane.

These conclusions are, of course, independent of whether the polymerization is stopped by combination of a polymerizing radical with a methyl radical, by combination of two polymerizing radicals, or by disproportionation between two polymerizing radicals.

Experimental Procedure and Calculations.

A mixture of peroxide and vinyl chloride of about the proportions corresponding to a typical kinetic run was prepared in bulb C and a run of 300 seconds duration at 158.5°C was made in the usual way using packed reactor #2. Ethane, vinyl chloride, peroxide and acetone were analyzed for. A second run was made

using the residual mixture in bulb C. The total pressure in bulb C is now less than it was for the first run but the proportions of the mixture will be the same. In the second run the mixture was allowed to expand into the reactor for 10 seconds and then immediately allowed to flow out again into bulb D for 10 seconds. Thus the effective reaction time is about 10 seconds and is negligible compared with the first run. No measurable acetone peak was found in the second run.

The calculation made from a typical experiment are as follows:

Run (1) 300 secs. reaction.

Total initial pressure in bulb C = 26.5 mm.

Product analysis:

Ethane	=	51.7×10^{12} molecules/cc. sec.
Vinyl Chloride	=	272×10^{15} molecules/cc.
Peroxide	=	240×10^{15} molecules/cc.
Acetone	=	228×10^{12} molecules/cc. sec.

Therefore the rate of addition of $\text{CH}_3\cdot$

$$\begin{aligned} &= 228 \times 10^{12} - (51.7 \times 10^{12} \times 2) \\ &= 1.25 \times 10^{14} \text{ radicals/cc. sec.} \end{aligned}$$

(From the peroxide and acetone recovered the peroxide initially present can be calculated to be 274×10^{15} molecules/cc..)

Run (2) negligible reaction.

Total initial pressure in bulb C = 23.6 mm.

Product analysis:

Vinyl Chloride	=	289×10^{15} molecules/cc.
Peroxide	=	243×10^{15} molecules/cc.

Thus if blank run had been carried out with the mixture used for

run (1) the analysis would have given:

$$\begin{aligned}\text{Vinyl Chloride} &= 289 \times 10^{15} \times \frac{265}{236} \\ &= 325 \times 10^{15} \text{ molecules/cc.}\end{aligned}$$

$$\begin{aligned}\text{Peroxide} &= 243 \times 10^{15} \times \frac{265}{236} \\ &= 273 \times 10^{15} \text{ molecules/cc.}\end{aligned}$$

If measurements are accurate this should equal the value of 274×10^{15} molecules/cc. calculated from Run (1). The difference is 0.4% which must be considered very good agreement.

Therefore the amount of vinyl chloride consumed in 300 seconds reaction time $(325 - 272) \times 10^{15} = 53 \times 10^{15}$ molecules/cc.

which corresponds to a rate of disappearance of vinyl chloride
 $= 1.77 \times 10^{14}$ molecules/cc. sec.

Therefore there are $\frac{1.77}{1.25} = 1.42$ molecules of vinyl chloride removed per methyl radical added.

Two other similar determinations gave values of 1.27 and 1.48 molecules of vinyl chloride removed per methyl radical added.

APPENDIX 3

Correction of Results by Comparison with Data on Ethylene Reaction.

As is mentioned on page 69 the function

$$R_X = R_{\text{acetone}} - R_{\text{CH}_4} - 2R_{\text{C}_2\text{H}_6}$$

is not equal to the rate of addition but can be related to it by the equation

$$R_{\text{addition}} = fR_X$$

where f is a function of the concentration of methyl radicals and also the concentration of vinyl chloride and will have a value between 0.5 and 1. In Table XVI, page 100, Brinton's results with ethylene are tabulated together with the calculated values of R_X . The function f , as calculated by two independent methods, is also tabulated where

$$f' = \frac{R_{\text{butane}} + 2.26R_{\text{hexane}}}{R_{\text{acetone}} - R_{\text{CH}_4} - 2R_{\text{C}_2\text{H}_6}}$$

$$f'' = \frac{R_{\text{butane}} + 2.26R_{\text{hexane}}}{2R_{\text{butane}} + 2.26R_{\text{hexane}}}$$

Average values of each of these functions for each temperature are also calculated. The values of $(2R_{\text{butane}} + 2.26R_{\text{hexane}})$ are tabulated beside the corresponding values of R_X .

In Fig. 19 (page 101) $(R_X/R_{\text{C}_2\text{H}_6}^{1/2})$ is plotted versus ethylene concentration and in Fig. 20 (page 102) the derived Arrhenius plot, on the assumption that $R_X = 2R_{\text{addition}}$, is shown. From this plot we obtain the rate equation

TABLE XVI

Application of Material Balance Method to Brinton's Data (14)
on Methyl Radical/Ethylene Reaction.

Temp. °C	C ₂ H ₄ conc. (a)	Brinton's Result $\frac{R_{add}}{R_{C_2H_6}^{\frac{1}{2}}}$ (b)	R _X	$2 \left(\begin{matrix} R_{butane} \\ + 1.13 R_{hexane} \end{matrix} \right)$ (c)	f'	f''	$\sqrt{\quad}$ x10 ¹¹
124	0.418	0.229	0.46	0.66	0.78	0.54	1.42
	1.200	0.636	1.36	1.48	0.64	0.58	1.10
	2.39	1.178	2.46	2.31	0.57	0.65	0.948
	3.67	1.648	3.16	2.52	0.54	0.67	0.856
	4.66	2.050	4.38	2.85	0.45	0.69	0.824
				Average	0.60	0.63	1.05
140	1.126	0.995	7.1	6.7	0.52	0.55	1.79
	2.31	1.905	11.2	10.8	0.57	0.60	1.72
	3.56	2.940	16.8	14.42	0.54	0.63	1.55
	4.40	3.385	19.8	15.26	0.49	0.63	1.45
				Average	0.52	0.60	1.63
159	1.155	1.526	40	30.2	0.40	0.54	3.44
	2.28	2.955	58	51.8	0.50	0.56	2.76
	3.45	4.420	83	70.2	0.50	0.59	2.67
	4.46	5.790	105	84.6	0.48	0.59	2.23
				Average	0.47	0.57	2.78

(a) molecule cm⁻³ x 10⁻¹⁷
(b) molecule^{1/2} cm^{-3/2} sec^{-1/2} x 10⁻⁶
(c) molecule cm⁻³ sec⁻¹ x 10⁻¹²

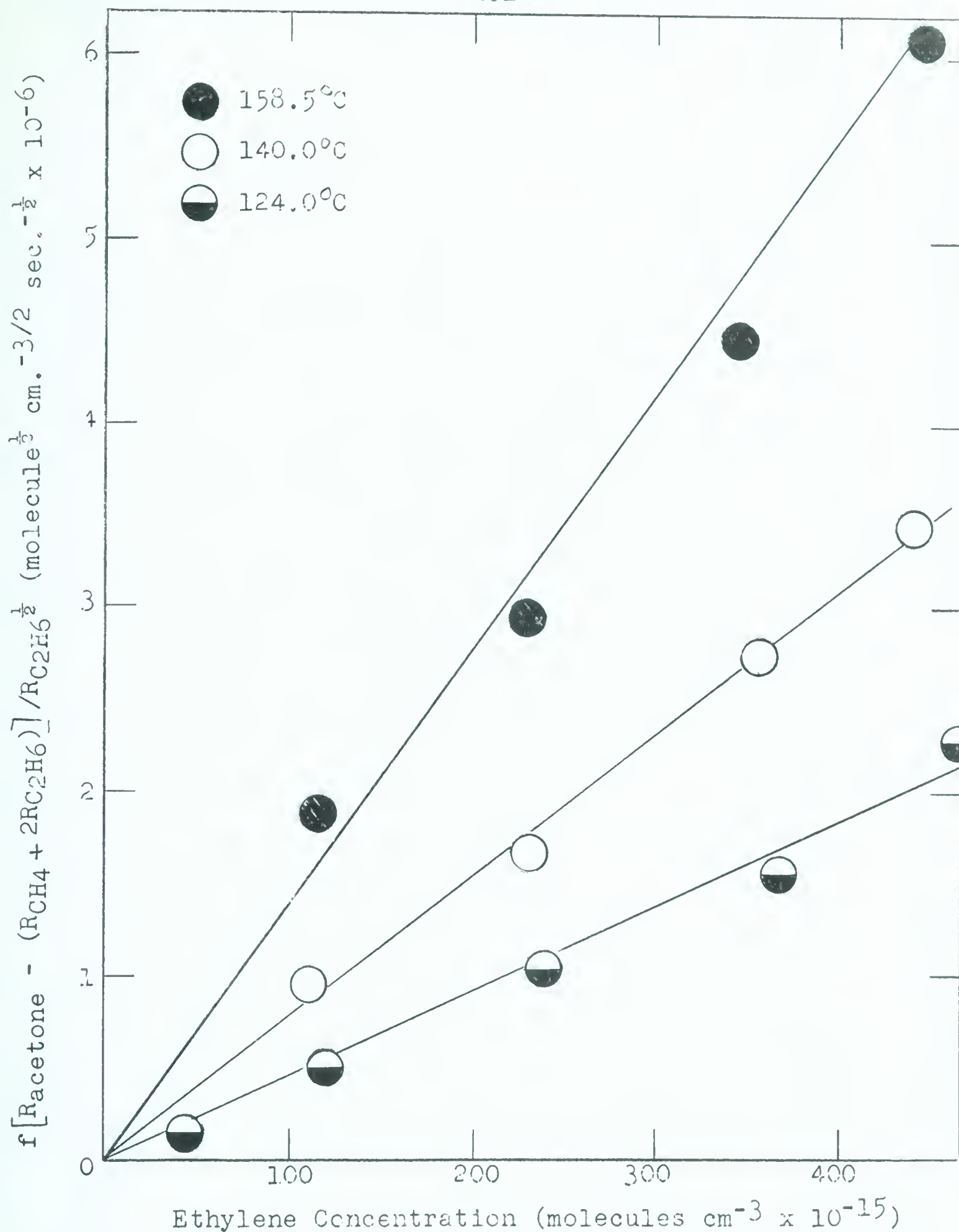


Fig. 19 Plot of $f[\text{Racetone} - (\text{RCH}_4 + 2\text{RC}_2\text{H}_6)] / \text{RC}_2\text{H}_6^{1/2}$ versus ethylene concentration from Brinton's data on methyl radical/ethylene reaction. $f = \frac{1}{2}$

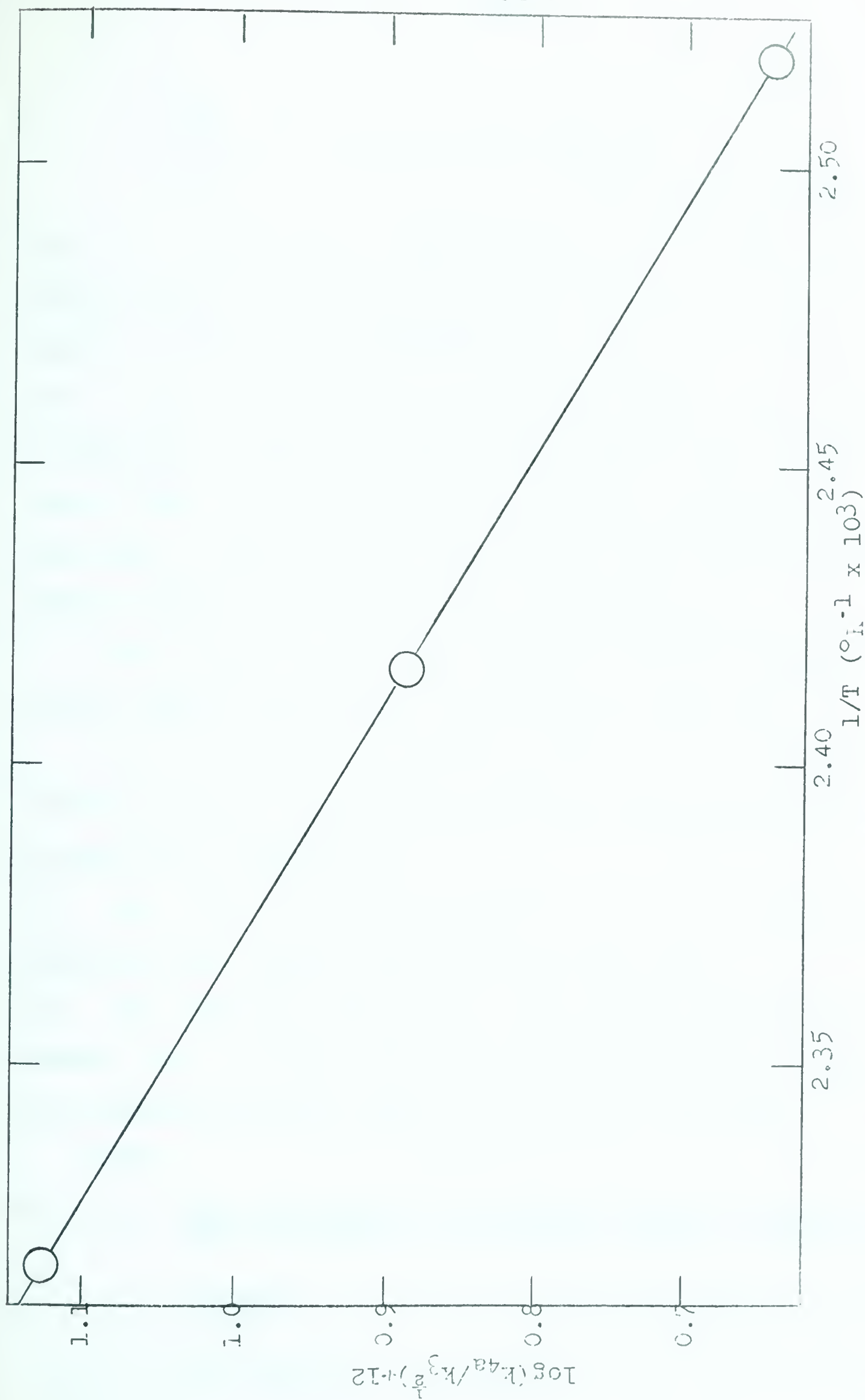


Fig. 20 Arrhenius plot: $\log(k_{4a}/k_3^{1/2})$ versus $1/T$ for Brinton's data on methyl radical/ethylene reaction. $f = \frac{1}{2}$

$$\frac{k_{4a}}{k_3^{1/2}} = 1.80 \times 10^{-6} e^{-10200/RT} \text{ cm}^{3/2} \text{ molecules}^{-1/2} \text{ sec}^{-1/2}$$

Thus it is seen that by using the material balance method, a very similar result is obtained as is from Brinton's total analysis method. $(0.33 \times 10^{-6} e^{-8860/RT})$ If we consider Table XVI, page 100, it will be seen that R_X is always greater than $2(R_{\text{butane}} + 1.13R_{\text{hexane}})$ indicating that either methyl radicals are disappearing by some other route than by addition, termination or methane and ethane formation or, alternatively, that some of the butane and/or hexane is not recovered during analysis.

The values of f , as calculated by the two methods, do not differ greatly but mostly lie between 0.5 and 0.6.

It is possible to arrive at values for f for the vinyl chloride system by comparison with the ethylene results if a few assumptions are made viz.

- (a) The rates of methyl radical/chlorovinyl radical and methyl radical/propyl radical reactions are the same.
- (b) The combined rates of all chloropropyl radical/chloropropyl radical and all propyl radical/propyl radical (i.e. combination and disproportionation taken together) are the same.

Thus:

$$\begin{aligned} \text{if } u &= \frac{\text{Rate of addition with double methyl disappearance}}{\text{Rate of addition with single methyl disappearance}} \\ &= \frac{R_{\text{butane}}}{2.26R_{\text{hexane}}} \quad (\text{in the ethylene reaction}) \end{aligned}$$

$$u = \frac{k_5(\text{Propyl})(\text{Methyl})}{k_6(\text{Propyl})(\text{Propyl})} \quad *$$

$$= \frac{k_5(\text{Methyl})}{k_6(\text{Propyl})}$$

Using the symbols

(P) = Propyl radical concentration

(M) = Methyl radical concentration

(E) = Ethylene concentration

k_a = Rate constant for addition of methyl to ethylene.
(Brinton's k_{4a})

we can write a steady state equation for propyl radicals.

$$\frac{d(P)}{dt} = k_a(M)(E) - k_5(M)(P) - k_6(P)^2 = 0$$

Therefore

$$(P) = \frac{-k_5(M) + \left[k_5^2(M)^2 + 4k_6k_a(M)(E) \right]^{1/2}}{2k_6}$$

Substituting in equation for u:

$$u = \frac{k_5k_6(M)}{k_6 \left\{ -k_5(M) + \left[k_5^2(M) + 4k_6k_a(M)(E) \right]^{1/2} \right\}}$$

$$\frac{1}{u} = \left(1 + \frac{4k_6k_a(E)}{k_5^2(M)} \right)^{1/2} - 1$$

$$\frac{4k_6k_a}{k_5^2} = \left[\left(\frac{1}{u} + 1 \right)^2 - 1 \right] \frac{(M)}{(E)}$$

* k_5 and k_6 are the rate constants for the propyl/methyl and propyl/propyl reactions respectively, the numeration being that used in Brinton's paper (14).

$$\frac{4k_6k_a}{k_5^2} = \left[\left(\frac{1}{u} + 1 \right)^2 - 1 \right] \frac{R_{C_2H_6}^{\frac{1}{2}}}{\frac{k_3^{\frac{1}{2}}(E)}{3}}$$

or $\Gamma = \left[\left(\frac{1}{u} + 1 \right)^2 - 1 \right] \frac{R_{C_2H_6}^{\frac{1}{2}}}{(E)} \quad \text{----- (a)}$

where $\Gamma = \frac{4k_6k_3^{\frac{1}{2}}k_a}{k_5^2}$

Total rate of addition, R_a , = Rate of addition with double methyl disappearance.
 Rate of addition with single methyl disappearance.

$$R_x = (R_{\text{acetone}} - R_{CH_4} - 2R_{C_2H_6}) = 2 \times \text{Rate of addition with double methyl disappearance.}$$

Rate of addition with single methyl disappearance.

$$u = \frac{\text{Rate of addition with double methyl disappearance}}{\text{Rate of addition with single methyl disappearance}}$$

$$\text{Therefore } R_a = \frac{(u+1)}{(2u+1)} (R_{\text{acetone}} - R_{CH_4} - 2R_{C_2H_6})$$

$$\text{and so } f = \frac{(u+1)}{(2u+1)} \quad \text{----- (b)}$$

Using equations (a) and (b) we can correct our result by determining the various values of f in the following manner:

In the ethylene system

$$\Gamma = \left[\left(\frac{2.26R_{\text{hexane}}}{R_{\text{butane}}} + 1 \right)^2 - 1 \right] \frac{R_{C_2H_6}^{\frac{1}{2}}}{[C_2H_4]}$$

and in Table XVI* calculated values of Γ for all Brinton's experiments with ethylene are listed Γ , being a function of several rate constants, should be constant at any one temperature. In fact the constancy is not very good but this may be attributable

* Table XVI, page 100.

to experimental error and so average values are calculated for each temperature.

Values of \bar{r} must now be calculated for the vinyl chloride system. According to the assumptions made at the beginning of this derivation, the only difference between the two systems will be the rate of addition of methyl radicals to the double bond and hence the k_a in \bar{r} .

Using the results for the rates of addition of methyl radicals to vinyl chloride obtained from Fig. 11 as a first approximation, we find the following ratios of $k_a(\text{vinyl chloride})/k_a(\text{ethylene})$:

Temperature (°C)	$\frac{k_a(\text{vinyl chloride})}{k_a(\text{ethylene})}$
122	10.35/5.6 = 1.84
139	19.00/9.1 = 2.09
159	29.49/13.4 = 2.20

Thus $\bar{r}_{122^\circ\text{C}}$	(vinyl chloride)	$1.84 \times 1.05 \times 10^{-11} = 1.93 \times 10^{-11}$
$\bar{r}_{139^\circ\text{C}}$	(vinyl chloride)	$2.09 \times 1.63 \times 10^{-11} = 3.41 \times 10^{-11}$
$\bar{r}_{159^\circ\text{C}}$	(vinyl chloride)	$2.20 \times 2.78 \times 10^{-11} = 6.11 \times 10^{-11}$

Using these values of \bar{r} (vinyl chloride) we can calculate the values of u from equation (a) in the form

$$u = \frac{1}{\left(1 + \frac{\bar{r}_{\text{vinyl chloride}}}{R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}}\right)^{\frac{1}{2}} - 1}$$

and hence f from equation (b).

These calculated values of f are listed in Table XI, page 66, to

gether with the corrected values of $R_{\text{addition}}/R_{\text{C}_2\text{H}_6}^{1/2}$ as previously mentioned.

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MASS SPECTROMETRY OF LYCOPODIUM ALKALOIDS.

INTRODUCTION

When mass spectrometers were first developed from the pioneer work of J. J. Thomson and others, research utilizing them was directed at the determination of the isotopic composition of elemental gases. When volatile compounds were investigated it was found that a spectrum of ions was detected corresponding in mass to that of the parent compound together with fragments consisting of groups of atoms present in the compound.

With the construction of stable modern mass spectrometers it was found that these "mass spectra" observed when compounds were studied were remarkably reproducible from instrument to instrument, provided the mass spectrometer was operated under fairly standard conditions i.e. the pressure in the source should be $<10^{-5}$ mm. and the ionizing electron energy about 70 ev..

The process resulting in the formation of a mass spectrum is visualized as follows. The interaction of the bombarding electron with the molecule leads to ionization (1a), (1b).



where positive molecular ions with varying degrees of vibrational and electronic excitation are formed. The highly excited molecular ions decompose unimolecularly in the ion source producing two or more fragments, one of which is an ion. Since the residence time in the ion source ($\sim 2-3$ microseconds) is comparatively long, further decomposition of the excited ionic fragments can

occur. The sum of the ionic species produced in this manner in the ion source is observed as the mass spectrum. Longer lived excited ions may decompose during the process of mass separation. In instruments using magnetic analysis, ions decomposing in the field free region after acceleration but before magnetic deflection can appear as diffuse peaks, called metastable peaks, at mass

$$m^* = \frac{m_2^2}{m_1}$$

where m^* refers to the m/e of the metastable peak, m_1 to the parent ion and m_2 to the daughter ion. These metastable peaks are useful in establishing the origin of ions in the normal mass spectrum.

The first reasonably successful interpretation and theoretical prediction of mass spectra was developed by Rosenstock (1) on the basis of the statistical absolute reaction rate theory. This statistical theory of mass spectra has been applied mainly to systems like propane (2,3,4), ethanol (5), methyl acetate (6), ethyl chloride (7), ethyl amine (7) and ethyl mercaptan (7).

The application of the theory is difficult and involves complicated calculations and, since a number of assumptions have to be made, leads often to uncertain results. For this reason it has not been applied as an aid in structural elucidation by mass spectrometry.

The empirical correlations of mass spectra of related compounds have been of much greater practical usefulness. Such an empirical approach often utilizes concepts obtained from the study of ionic reaction mechanisms in solution, that is concepts

developed in the field of physical organic chemistry. Correlations of this type are often observed to hold and it will be useful to compare the basic features of ionic solution reactions and fragmentations in the ion source of a mass spectrometer.

The moderate temperatures used in solution reactions require that the activated complex is one of low, or lowest possible, energy. While a low activation energy is also of importance in determining the abundance of a given fragment ion in the mass spectrum, as is evident from the approximate formula of Rosenstock et al. (1),

$$k = Z \frac{(E - E_0)^{N-1}}{E}$$

for simple bond rupture where Z is a frequency factor, E_0 is the activation energy, and N is the number of internal degrees of freedom of the ion. A number of important differences must be expected to exist between reaction mechanisms in the ion source and in solution. Two of the most important reasons for this are: (a) the amount of available excitation energy is much greater in ions produced by 70 ev. electron bombardment than in those produced in solution (b) solvation effects are present in solution but not in low pressure gas.

Thus a certain amount of caution must be exercised in transferring concepts from physical organic chemistry to mass spectrometry.

Nevertheless the conclusions on the stability of ions arrived at from solution work and theoretical organic chemistry have proved very useful in the qualitative interpretation of mass

spectra.

The complexity of the mass spectrum of an organic molecule increases rapidly with the number of atoms present and early attempts to characterize the fragment ions present and to explain their origin indicated that while mass spectrometry was a very sensitive method for detecting small quantities of organic compounds and identifying them by comparison with the mass spectra of a known sample, little information could be derived as to the structure of an unknown compound. The molecular weight could usually be derived from the last major peak on the spectrum (i.e. neglecting isotope peaks) but in some cases it was found that this "parent" or "molecular" peak was absent and in a few cases a peak one mass unit higher than the molecular peak, corresponding to a protonated molecular ion produced by collision within the source, was of greater intensity than the molecular ion. Also the compounds which could be investigated had to be sufficiently volatile so that the required pressure could be maintained in the ion source. This limited the usefulness of the mass spectrometer as an analytical tool particularly in the field of natural product chemistry where molecules encountered are frequently very large and involatile. Since natural products are often isolated in very small samples an analytical tool which can gain information while consuming only trace quantities of material is very valuable in their study. If the problems of their low volatility and the complexity of the resultant data could be overcome, the mass spectrometer is obviously such an analytical tool.

Recently commercial mass spectrometers with heated inlet systems have become available which can operate at temperatures as high as 400°C and so compounds of low volatility can be studied provided they have moderate thermal stability. The problem of the complexity of the mass spectral data can be approached by the empirical method of studying a series of compounds of a particular group and developing "rules" which can be applied to the structural elucidation of other members of the group. Unfortunately it appears that very few rules can be carried over from one group of compounds to another and it is not likely that in the near future an adequate theoretical approach will be developed which can predict the cracking pattern of a complex organic molecule.

In the investigation which is reported here the method of formulating rules from the examination of the mass spectra of known compounds in a group and extending them to the structural elucidation of unknown members of the same group was applied to alkaloids of the Lycopodium group.

The alkaloids studied were provided by Dr. W. A. Ayer and Mr. D. A. Law in conjunction with whom the investigation was undertaken.

The contribution of the author was confined to the assembly of the heated inlet system, the obtaining of the mass spectra and the subsequent interpretation of these spectra.

EXPERIMENTAL

The instrument used in this investigation was an A.E.I.M.S.2 mass spectrometer, a magnetic focussing 60° sector instrument. Before it could be used for high molecular weight material it was modified to bring it up to M.S.2-H specifications which involved the addition of a heated inlet system, which was constructed principally of glass, and an electrostatically variable collector slit which allowed resolution of ions up to the mass 400 region.

The heated inlet system (Fig. 1, page 206) consists essentially of a 300 cc. glass flask with incorporated Metrosil (metallic sinter) disc leak surrounded by heaters and insulating material (1-2 mm. glass beads) contained in a metal cylinder. Gas flow is controlled by a three way valve system which consists of three steel shafts with hardened steel spherical ends attached to a bellows arrangement which allows a screw movement to firmly seat the spherical end of the shaft in the appropriate hole in an "interspace block". Most of the metallic surfaces which would come into contact with the sample are "vitreous enamelled" to minimize catalytic decomposition. All vacuum seals in this system are by means of gold gaskets (0.020 in. diameter wire). One of the valves opens to a pumping lead which goes through a liquid nitrogen trap via an oil diffusion pump to a rotary backing pump. A second valve leads to a pyrex sample bottle which is attached to the system by a brass nut and sealed with a gold gasket. The sample bottle can be heated by means of a glass bead packed, electrically heated furnace which can be raised or lowered. The third valve opens into the flask.

τ Indicates location of thermocouple

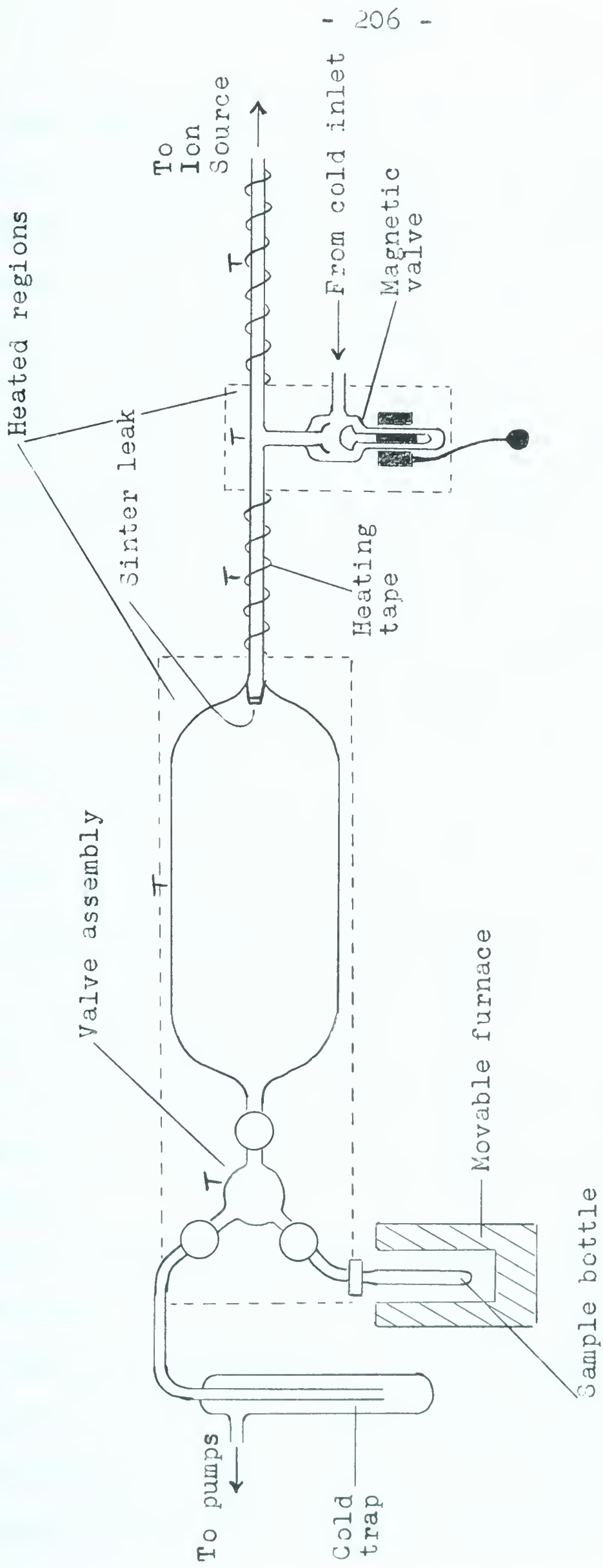


Fig. 1 Heated Inlet System

From the metrosil leak a glass tube leads to an all glass magnetic valve and a further glass tube leads directly into the ionization chamber. These tubes are heated by means of electrical heating tapes and the magnetic valve by heating collars on a brass casing which surrounds it.

The purpose of the magnetic valve is to shut off the copper pipe lead to the cold inlet system so that high molecular weight compounds being introduced via the heated inlet system may not back up into this cold pipe and condense. Thermocouples attached to the system at several points are connected via a multiple throw switch to a galvanometer calibrated in degrees centigrade above room temperature. The heaters are controlled by a number of autotransformers.

The method of sample introduction is as follows:

With the "flask" and "sample" valves closed and the "pump" valve open, the sample bottle is removed and a small amount of sample placed in it. The sample bottle is reconnected and the "sample" valve opened to exhaust the air (if the sample is volatile it can be cooled in liquid nitrogen during this operation but none of the alkaloids used in this study required such treatment).

The "flask" valve is now opened and the "pump" valve closed. By "sitting" on the 28 peak (or by observing the total ionization gauge which is connected by a second amplifier to the first collimating plate in the ion source) any air leak can be detected and corrected before continuing. The furnace is now raised around the sample bottle and the sample evaporated until a deflection on

the total ionization gauge corresponding to a suitable sample pressure is obtained. The "flask" valve is now shut and the "pump" valve opened. The total ionization will not now decrease appreciably over the hour or more required for a scan of the mass spectrum.

A few samples were introduced into the ion source without passing through the sinter leak using the apparatus shown in Fig. 2 (page 209). Samples were sealed into the evacuated break-seals and with the filament turned off in case of accident a breakseal was broken. When it was seen that no air leak had developed during this procedure, the filament was turned on again and the sample heated gently by means of an electrically heated air bath. The temperature of the manifold and connection to the ion source was maintained at a slightly higher value by means of heating tapes. When a suitable sample pressure was obtained, the air bath was allowed to come to equilibrium and a scan made. It was found that if doors and windows were shut, no elaborate thermostating device was required over the time needed for a scan. By this means scans could be taken at much lower temperatures ($<70^{\circ}\text{C}$) in a system which had absolutely no metal outside the ion source.

The assembly of the apparatus requires that the vacuum in the tube be broken and hence that the machine be shut down. Since the mass spectrometer was in daily use for routine analytical work using the cold inlet system, it was not possible to conduct more than one set of experiments by this method.

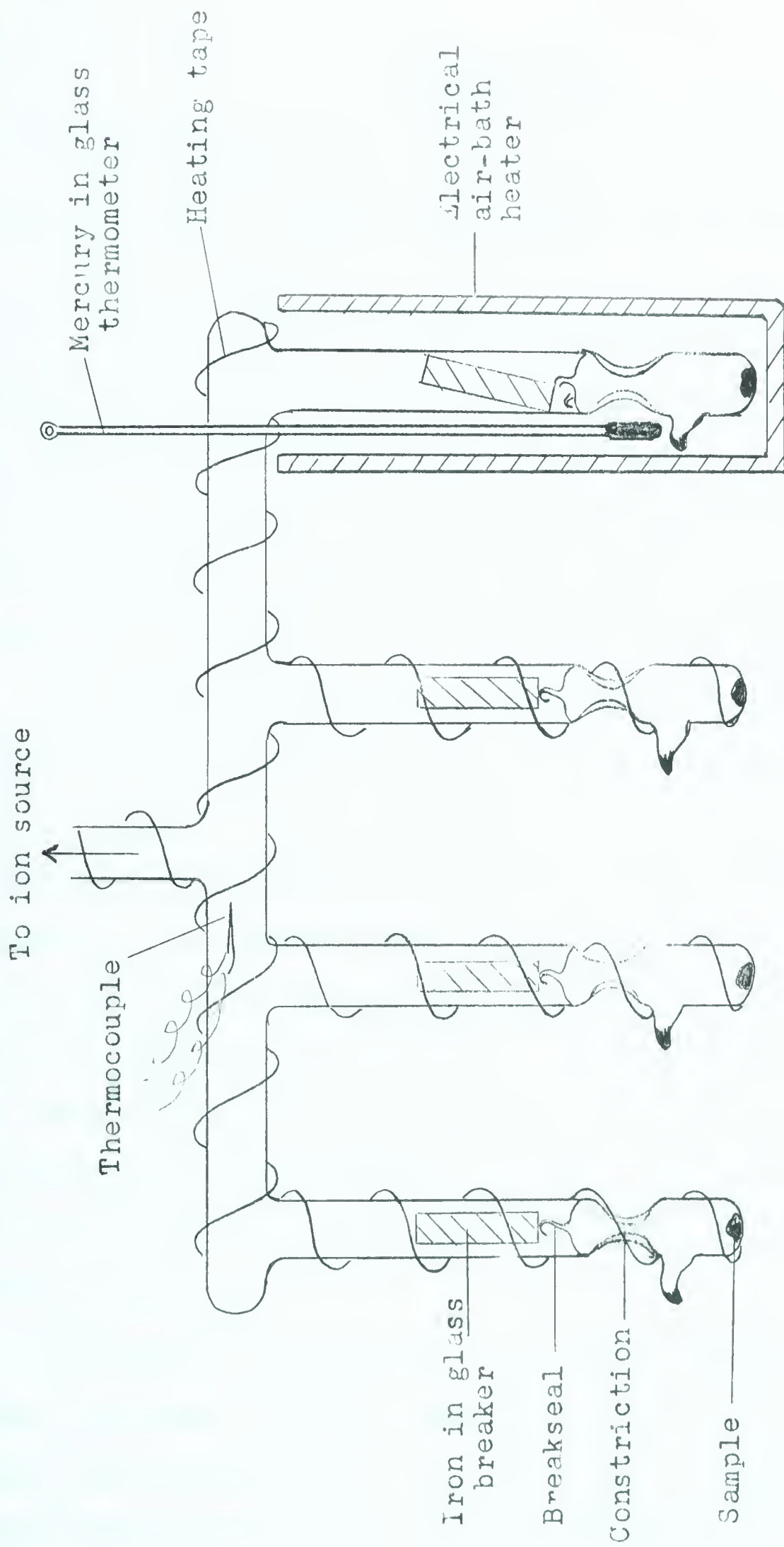


Fig. 2 Direct Inlet System

NOMENCLATURE

Before discussing the mass spectra of the alkaloids studied it will be best to define the nomenclature which will be used.

The ion produced by loss of one electron from the compound will be referred to as the "molecular ion" and the corresponding peak on the spectrum as the "molecular peak" or, more concisely, by the symbol M. Other peaks in the spectrum will be referred to either according to their mass to charge ratio (m/e) e.g. "the 190 peak" or according to the number of mass units by which they are less than the molecular ion e.g. "the M-57 peak".

In reporting the mass spectra all the peaks over $m/e=25$ were measured and their total height determined. This is essentially a measure of the total ion current because peaks below $m/e=25$ do not constitute more than a few percent of the ionization. Following the symbolism used by Biemann (8) we will designate the sum of the peak heights starting the count at $m/e=25$ as \sum_{25} and all individual peak heights are converted to a percentage of this, $\% \sum_{25}$, and are tabulated as such. For brevity if the 190 peak referred to above is 36.2% of the total ion current, we will designate it as the 190(36.2%) peak or alternatively the M-57(36.2%) peak.

Reference will be made from time to time to metastable peaks. These are small diffuse peaks produced by the collection of ions which are produced by the dissociation of larger ions after they have been accelerated and before they have been deflected by the magnetic field. The theory of the production of these peaks can

be found in any textbook of mass spectrometry (9) and their m/e can be determined fairly accurately from the formula

$$m^* = \frac{(m_2)^2}{m_1}$$

where m^* refers to the m/e of the metastable peak, m_1 to the parent ion and m_2 to the daughter ion. It can be seen that m^* will be less than either m_1 or m_2 . Such a metastable transition will be reported as e.g. $247 \longrightarrow 190(m^* = 146.2)$

Reporting of Experimental Data.

The mass spectra of the alkaloids studied are tabulated at the end of this report. These tables list m/e and $\% \sum_{25}$ which is considered to be a more useful form for comparative purposes than the more conventional m/e and Percentage of Base Peak*, due to the fact that the total ionization of isomeric compounds and compounds of similar structure and molecular weight does not change appreciably from compound to compound. In making comparisons between spectra in this investigation, m/e was plotted versus $\% \sum_{25}$ on strips of graph paper using a scale of 1 cm. = 10 m/e units and 1 cm. = 10% \sum_{25} . Such graphs are, however, too large to be included at their original scale. A few reduced graphs of typical spectra are shown in Fig. 3 (page 212) but they are not considered suitable for comparative purposes as it would obviously be impracticable to plot spectra of compounds to be studied in the future on exactly the same scale.

* Base Peak - most intense peak in the spectrum. E.g. in Lycopodine the 190 peak would be represented by 100%.

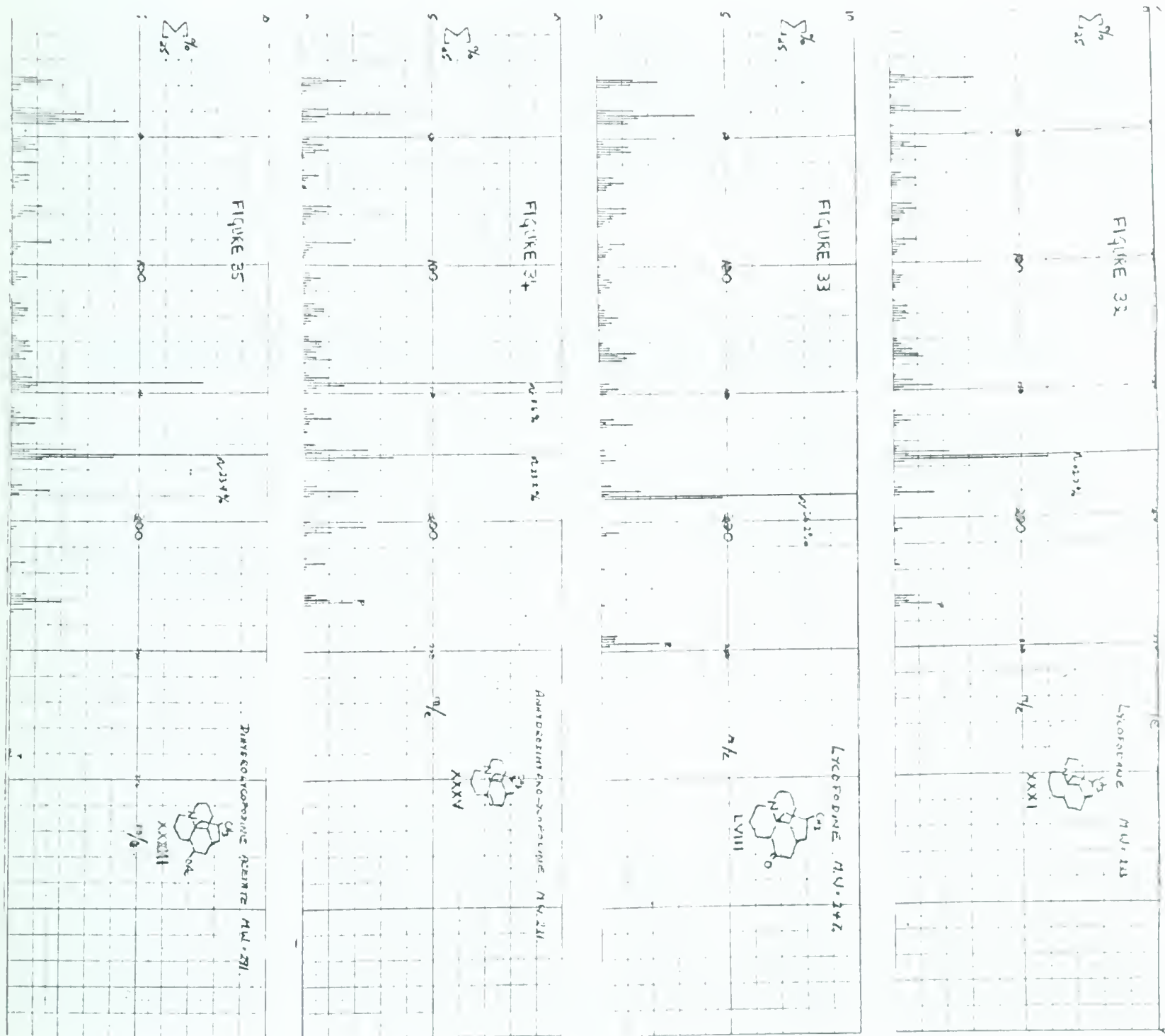
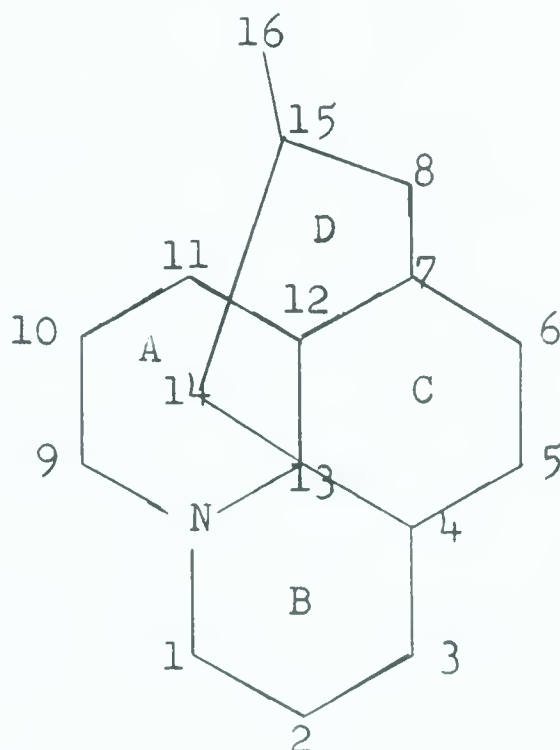


Fig. 3 Reduced graphs of typical spectra.

The chief value of the work reported here will be to give rules, based on the interpretation of the mass spectra of many characteristic alkaloids, by which the mass spectra of unknown alkaloids of related structure may be interpreted. It is for this reason that the values for m/e and $\% \sum_{25}$ are tabulated in full and it is suggested that anyone using these in further research should plot them on graph paper on a scale at least as large as the one quoted above.

Nomenclature Used in Discussing Lycopodine-type Skeleta.

The numbering system for the carbon atoms and the designation of the four rings in the basic skeleton found in most of the alkaloids discussed here can be illustrated for lycopodane.



GENERAL BIBLIOGRAPHY

In this report specific references are given infrequently. General information can be obtained from the following sources:

The actual mass spectra of various compounds have usually been obtained by a number of independant groups and can be found in several compilations of mass-spectral data. Perhaps the most exhaustive, although as yet poorly indexed, is the series issued by the American Petroleum Institute.

When information is required on the theory of mass spectrometry and details of the construction of various types of instrument perhaps the best source is "Mass Spectrometry and its Application to Organic Chemistry" by J. H. Benyon, although numerous other textbooks exist.

In the specialized field of interpretation of mass spectra in terms of the structural features of complex organic compounds, there have been several books published recently which have attempted to correlate the increasing numbers of results on different classes of compounds. While all have considerable merit, a certain amount of personal preference for the format adopted and the ease of obtaining information on a specific subject will make some appeal more than others. In the author's opinion "Interpretation of Mass Spectra of Organic Compounds" by H. Budzikiewicz, C. Djerassi and D. H. Williams is the most useful.

Because these books are all recently published and contain extensive bibliographies, they will be referred to in preference to the original papers. A few such texts are:

Theory of Mass Spectrometry.

J. H. Benyon "Mass Spectrometry and its Application to Organic Chemistry" Elsevier, Amsterdam, 1960.

F. H. Field and J. L. Franklin "Electron Impact Phenomena" Academic Press Inc., New York, 1957.

C. A. McDowell (ed.) "Mass Spectrometry" McGraw-Hill, New York, 1963.

Interpretation of Mass Spectra on Structural Basis.

H. Budzikiewicz, C. Djerassi, D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds" Holden-Day Inc., San Fransisco, 1964.

K. Biemann "Mass Spectrometry" McGraw-Hill, New York, 1962.

F. W. McLafferty "Mass Spectral Correlations" American Chemical Society, Washington, D.C., 1963.

RESULTS AND DISCUSSION

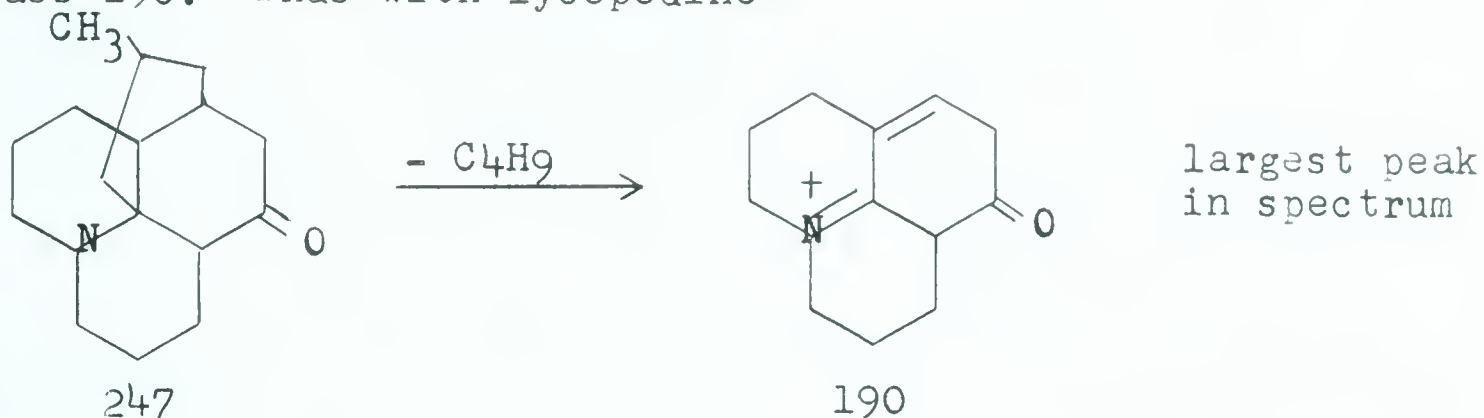
The spectra of the alkaloids studied were found to fall into several definite groups according to the basic skeleton of the compound and it is perhaps best to discuss each of these groups in turn. By far the largest proportion of the alkaloids examined had lycopodine-type skeletons and so we will first consider these compounds.

Alkaloids with Lycopodine-type Skeletons.

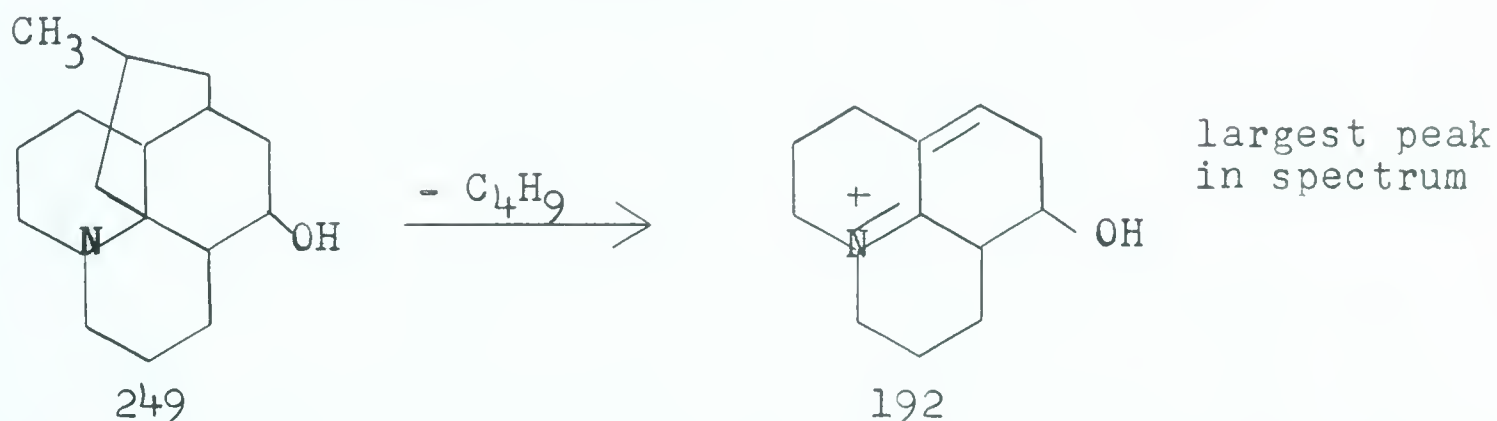
The principal features of the spectra are:

- (a) A region below $m/e = 140$ which is very similar for all alkaloids with this skeleton. The peaks are in groups with high intensities at $m/e = 41, 55, 67, 77, 79, 91, 120$ in most cases although individual alkaloids may have low intensities at one or other of these masses and have other major peaks in this region. A comparison of the spectra will show that this similarity does not extend to the alkaloids studied which have different basic skeletons. While it is not possible at this time to explain the modes of fragmentation which give rise to these characteristic peaks, from the spectra available we can conclude that this part of the spectra can be considered a "fingerprint" region by which any alkaloid with the lycopodine-type skeleton can be recognized.
- (b) Above $m/e = 140$ the spectra are unique for the alkaloid studied. Several features however are common to many of the cracking patterns. In lycopodine itself and many other of the related alkaloids the most intense peak is due to the loss of

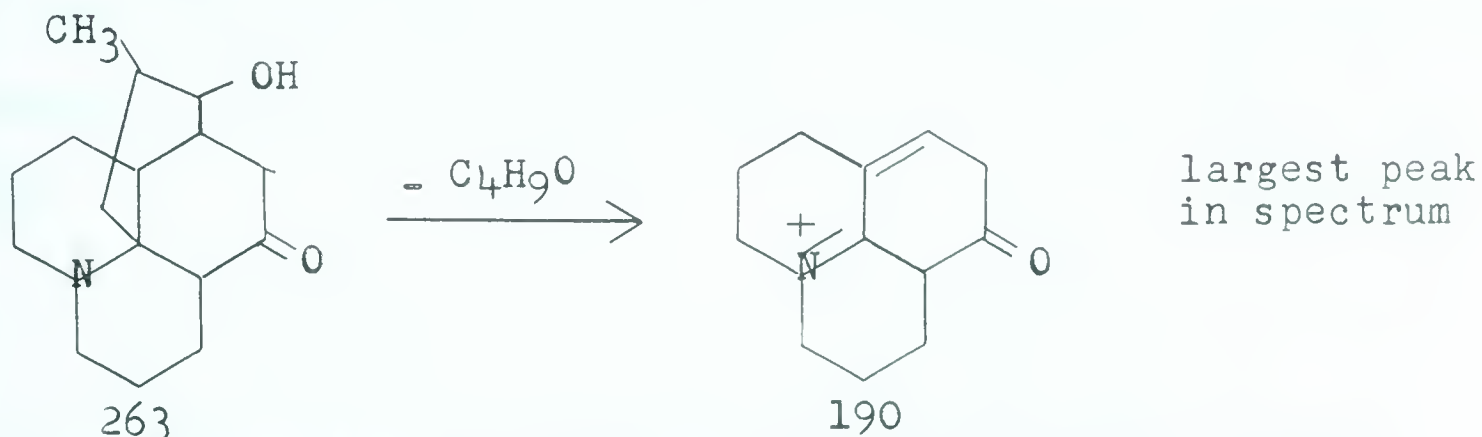
57 mass units and this corresponds to the loss of the "bridge" ring and a hydrogen atom from C₁₂ to give the very stable ion of mass 190. Thus with lycopodine



Similarly with dihydrolycopodine



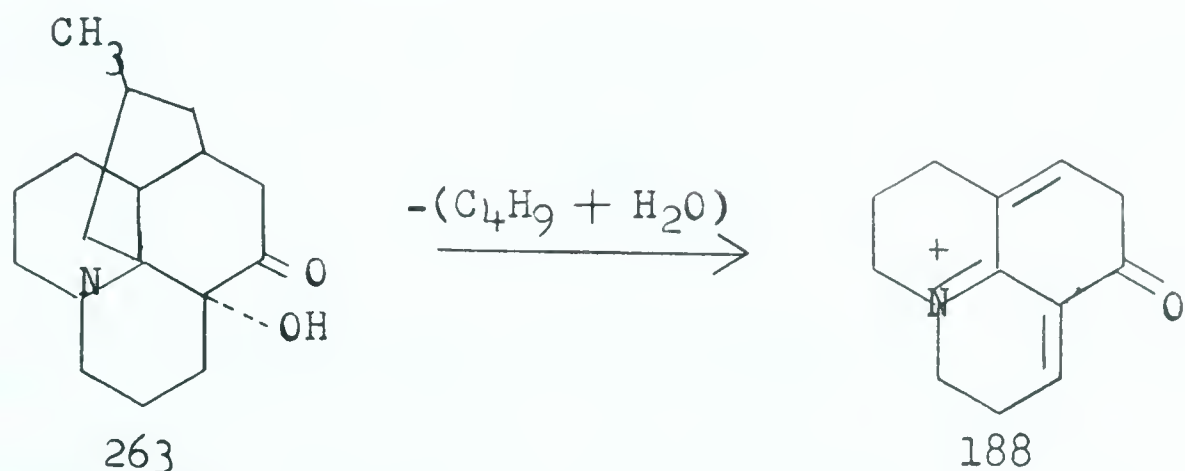
Substituents in the bridge ring do not appreciably affect this mode of fragmentation thus with clavolonine:



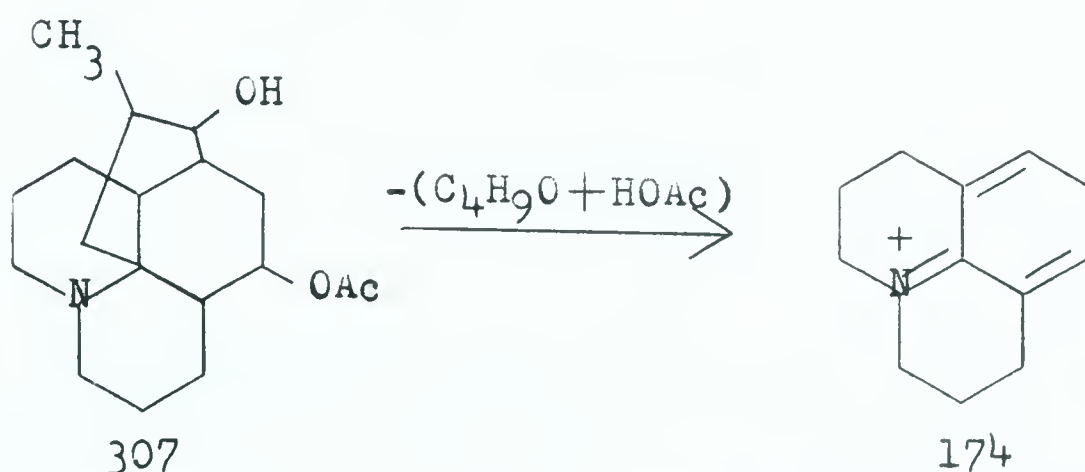
While this loss usually gives rise to the most intense fragment in the spectrum, if the molecule has an -OAc or -OH group present, the loss of C₄H₉ (or C₄H₉O) may be accompanied by the loss of H₂O or AcOH*

* Perhaps some of the loss of H₂O and AcOH is due to pyrolysis in the inlet system but it appears certain that the majority of it occurs during ionization. This conclusion is reached from the study of samples introduced by a low temperature admission system which will be discussed later (page 246).

e.g. Flabelliformine.

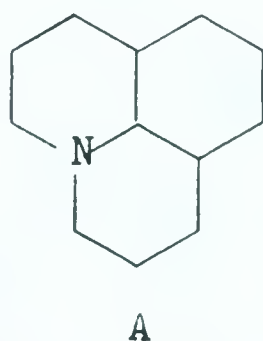


and Lofoline

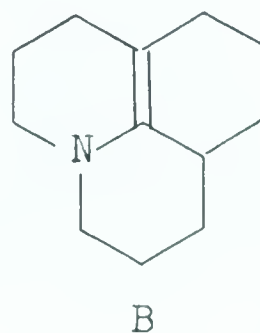


Verification of the structure of these ions can be obtained from two sources.

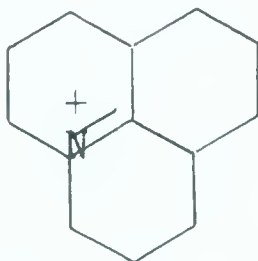
(a) The hypothesis that the positive charge is localized on the nitrogen is supported by examination of the two synthetic compounds



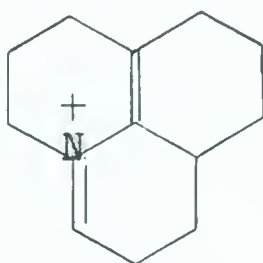
and



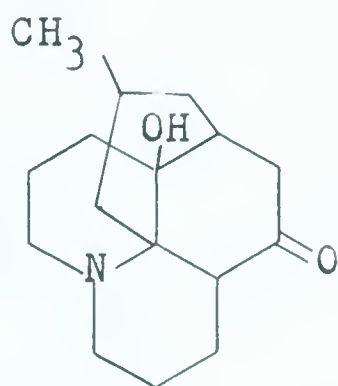
In A the M-1 peak accounts for 88.7% of the total ion current, indicating the very easy cleavage of the tertiary bond on C₁₃ to give the ion



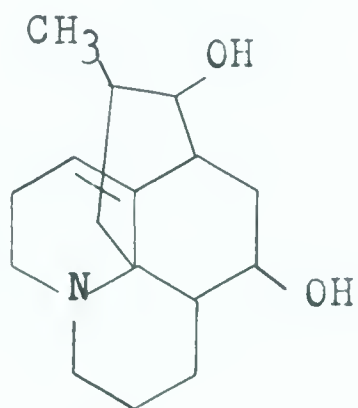
while in B, where there is no hydrogen on C_{13} , the M-1 peak accounts for only 13.7% of the total peak height presumably due to the ion



(b) In lycodoline, which differs from lycopodine in that the hydrogen on C_{12} is replaced by a hydroxyl group, the 190 peak is only the third most intense, exceeded in intensity by the molecular peak and 246 (M-17). In acrifolinol, which has a C_{11} , C_{12} double bond, the 192 peak, which would be expected from the loss of the bridge ring, is less than 3% of the total ionization.



Lycodoline

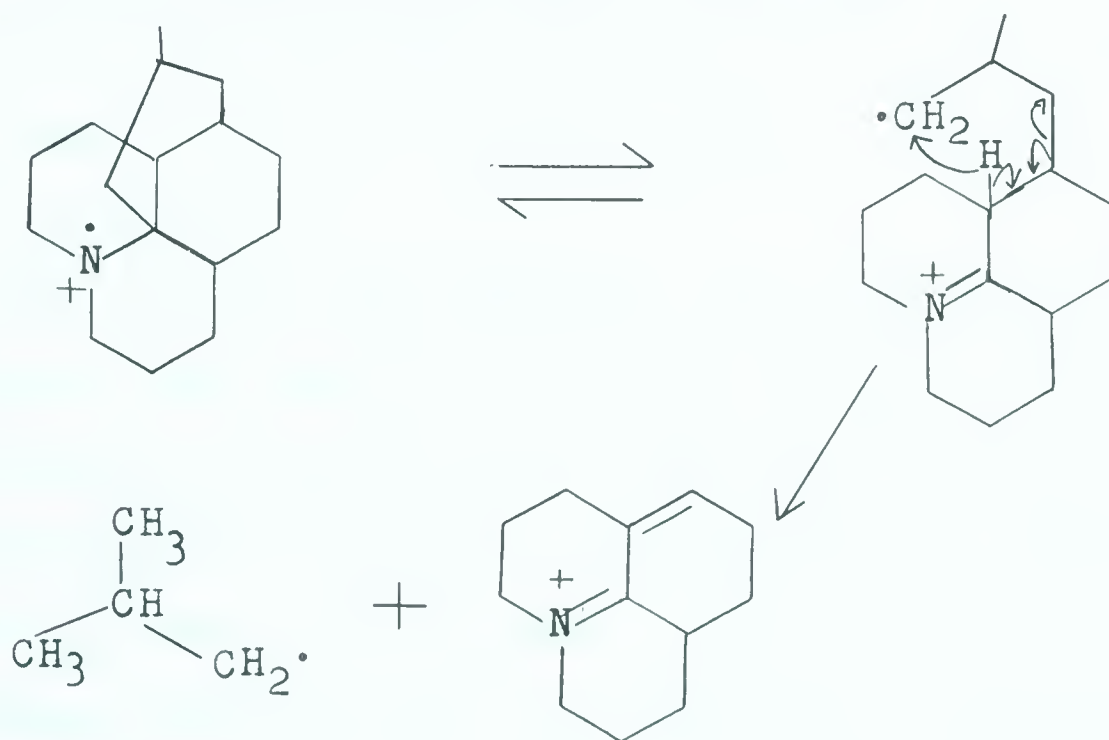


Acrifolinol

This supports the assumption that the C_{12} hydrogen is the one lost in conjunction with the bridge ring.

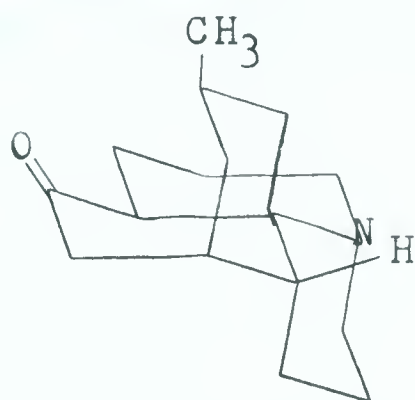
A metastable peak corresponding to a concerted loss of the bridge and the C₁₂ hydrogen from the molecular ion is found in all spectra where this typical fragmentation occurs. For example in lycopodine we find a metastable peak at approximately m/e = 146.5. The 247(M) \longrightarrow 190 + 57 transition would be expected to give a metastable peak at m/e = 146.1 which is in good agreement. However if the C₁₂ hydrogen was initially lost and the bridge lost subsequently in a separate fragmentation, that is the transition to the 190 peak was 246(M-1) \longrightarrow 190 + 56, the metastable peak expected would be at m/e = 146.8. Usually the simple formula for calculating the position of metastable peaks gives a value slightly lower than the experimental value* and so a concerted elimination of 57 mass units rather than a step-wise elimination of 1 and later 56 units is indicated.

Mechanistically this can be written:

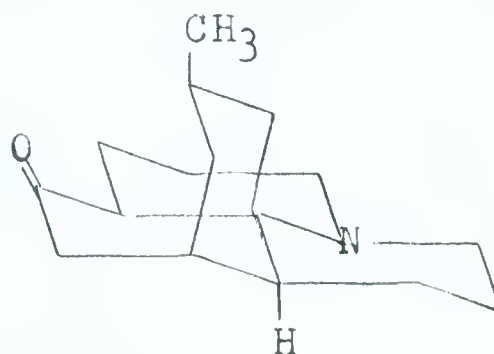


* See page 248.

In lycopodine the hydrogen on C₆ and the bridge ring are cis to one another which will, of course, favour the concerted mechanism. However in the isomeric epilycopodine the hydrogen and the bridge are trans to one another and such a mechanism should be expected to be greatly hindered.



Lycopodine



Epilycopodine

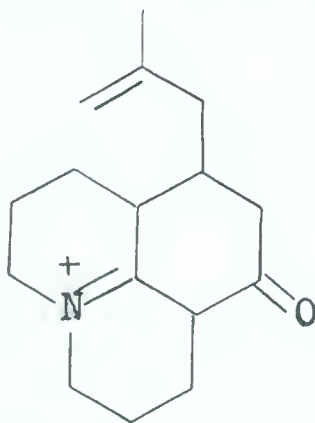
In lycopodine, the 190 peak is 36.2% of the total ionization while in epilycopodine it is only 20.6%. Although this supports the concerted mechanism, the steric effect is smaller than might be expected in a normal chemical reaction, illustrating the danger of applying normal criteria for chemical reactions to the reactions of highly energetic species in the ion source of a mass spectrometer.

This "bridge plus hydrogen" loss with or without accompanying H₂O or AcOH losses is the most striking feature of all lycopodine-type alkaloids where a hydrogen is present on C₆ and it should be possible from the examination of a relatively small number of peaks in the high m/e region of the mass spectrum of an unknown alkaloid with this skeleton to determine whether -OH or -OAc functions are present in the non-bridge moiety of the molecule. We will return to these important conclusions when we list "rules" for the interpretation of unknown spectra and when

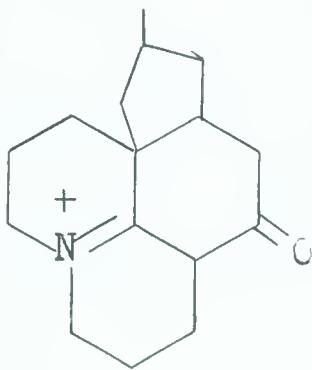
the spectra of various unknown alkaloids are discussed.

Turning now to the other principal peaks in the region $m/e = 140-247$ in the lycopodine spectrum, we find that the 246 peak is about 0.5% indicating a fairly favoured loss of a single hydrogen atom.

The most likely structure for this ion is

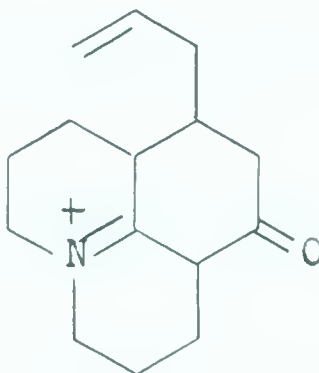


One other plausible structure

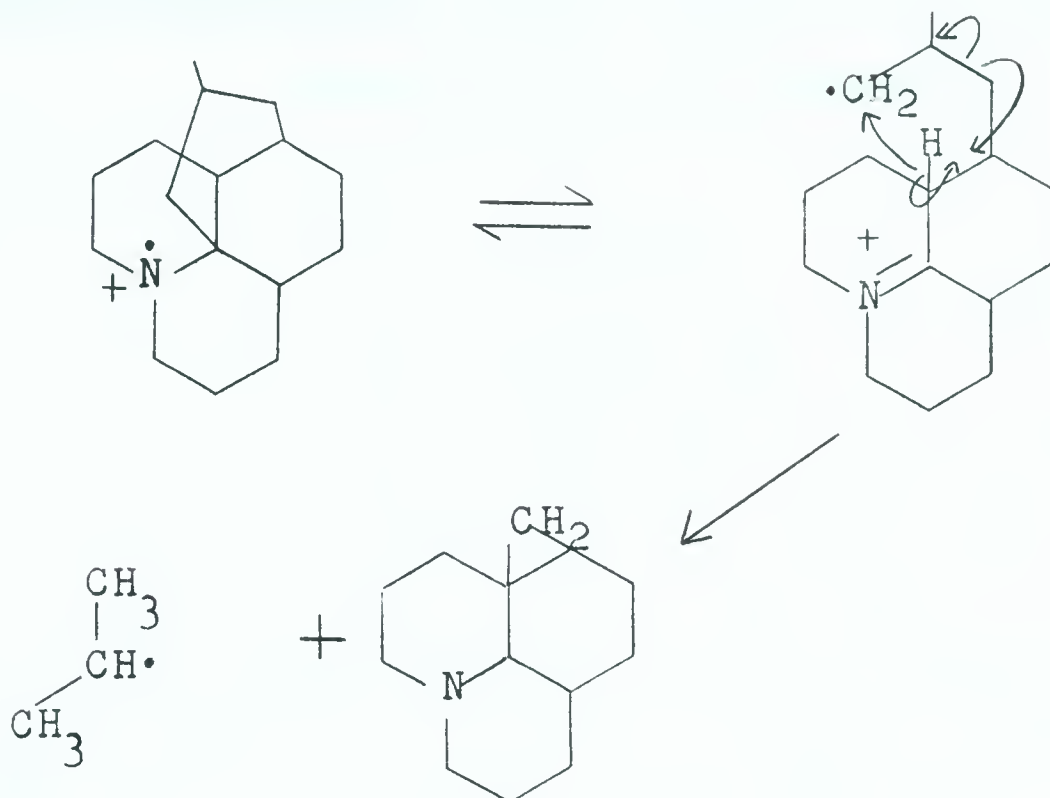


could only be considered correct if lycodoline and acrifolinol showed little or no M-1 peaks but this is not the case ($M-1_{\text{lycodoline}} = 0.61\%$, $M-1_{\text{acrifolinol}} = 0.99\%$).

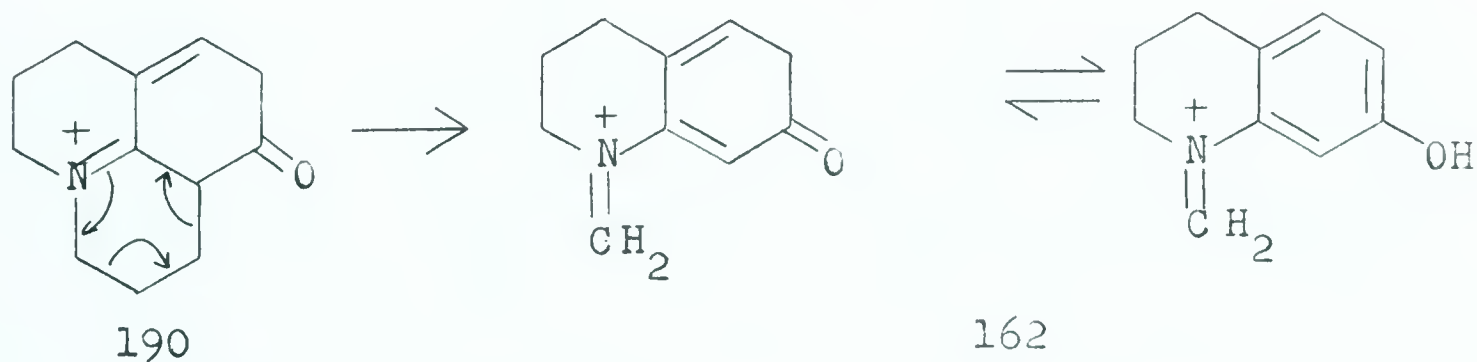
The 232, M-15 (0.18%) peak is obviously due to $-CH_3$ loss and its structure is probably



The peak at 204(0.79%) could be derived from the molecular ion by the mechanism



Peaks at m/e 28 units less than each of these four peaks are evident and the most likely explanation of this is loss of ethylene by a "reverse Diels-Alder" mechanism; a favoured method of fragmentation which is well established (10). Thus the 162 (1.32%) ion can be derived from the 190 ion

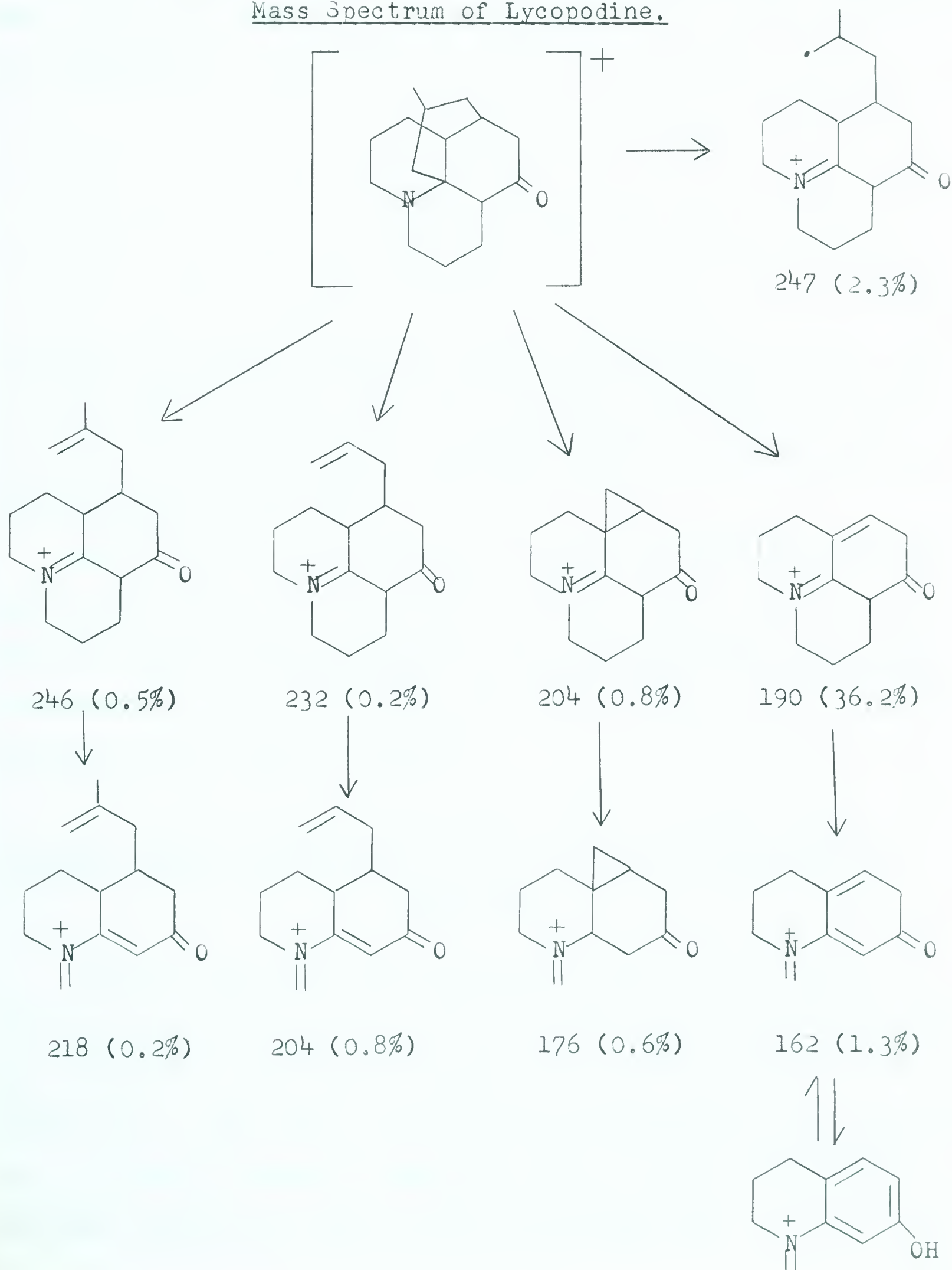


In Fig. 4 (page 224) a diagram of these modes of fragmentation for lycopodine is shown.

It will be noted that the 204 peak probably has contributions

Fig. 4

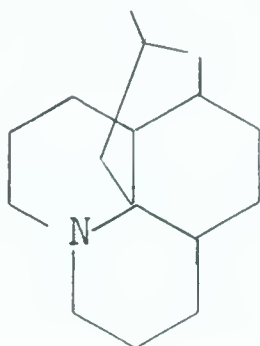
Probable Fragmentation Routes Leading to the Larger Ions in the
Mass Spectrum of Lycopodine.



from two different ions.

In lycopodine, the possibility exists that the loss of 28 mass units might be due to CO being eliminated by some mechanism.

In lycopodane



however, an exactly analagous fragmentation pattern obtains and in this case CO elimination is impossible. It seems reasonable to expect that the carbonyl function remains in the ions with masses greater than 162.

Below 162 the spectrum of lycopodine is difficult to interpret and, while structures could be drawn for the major ions, they all would involve migration of H or other groups and such conjecture without detailed evidence based on deuteration studies would be of no value whatsoever.

General "Rules" Governing the Mass Spectra of Lycopodine-type Alkaloids.

Several empirical rules can be arrived at by a survey of the spectra reported here. While no theoretical explanation will be attempted to account for these, no exceptions have so far been found and so they are of value in the examination of the spectra of an unknown compound. Combining these with the conclusions already reported we can list the following rules.

Loss of bridge ring D, together with its substituents, and the hydrogen on C₁₂ is the most favoured fragmentation. This does not apply when there is no H on C₁₂.

Loss of ethylene, probably involving C₂ and C₃, leads to peaks 28 mass units below peaks due to bridge loss or other favoured fragmentation.

Loss of H₂O from hydroxylated compounds and AcOH from acetates gives peaks 18 and 60 mass units respectively below other prominent peaks.

Loss of -CH₃ is common to all the alkaloids studied. Absence of such a peak would probably indicate that no methyl group is present in the molecule, but no such alkaloid has been studied.

Loss of -OH occurs in alkaloids containing this group to give an M-17 peak. This, however, is not specific for hydroxyl groups unless it is accompanied by M-18 and M-19 peaks. The relative intensities of these three peaks vary from compound to compound.

Acetates give very small parent peaks or none at all. They give peaks at M-59, M-60 and M-61 but there is never a peak at M-58. It is relatively easy to identify the peak corresponding to M-59 by observing these rules and hence the parent peak and from it the molecular weight. All acetates have a peak at mass 60 (except enol acetates) but none of the other alkaloids have measureable peaks at this mass.

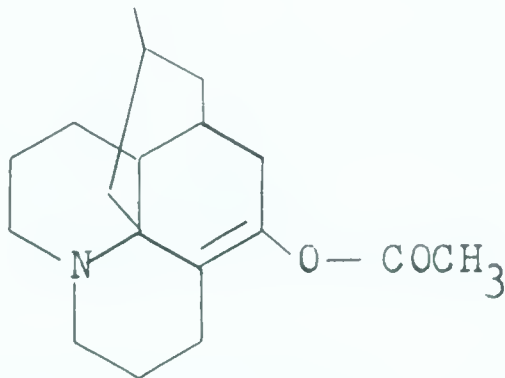
Although only two methyl esters (annopodine and lyconnotine) have been studied and both of these are not completely

characterized, it appears that the presence of a peak at mass 59 is indicative of a methyl ester grouping. This "rule" is in agreement with the spectra of aliphatic carboxylic acid methyl esters.

The alkaloids studied frequently lose two hydrogen atoms, presumably to form a double bond in one of the rings, and so most major peaks have a "shadow" peak at m/e two mass units less. This is particularly true of the molecular peak and it has been found that this effect increase with the length of time the sample has remained in the heated inlet system. Experiments with lower temperature direct admission of compounds to the ion source reduced the effect considerably and so it is probably principally due to pyrolysis in the heated inlet system.

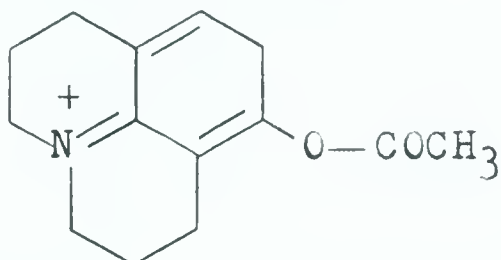
The modes of fragmentation discussed above account for the majority of the prominent peaks in the spectra of alkaloids with a lycopodine-type skeleton and no attempt will be made to discuss those alkaloids whose spectra can be considered "typical". There are, however, many spectra which show unusual features and these will now be treated individually.

Lycopodine Enol Acetate



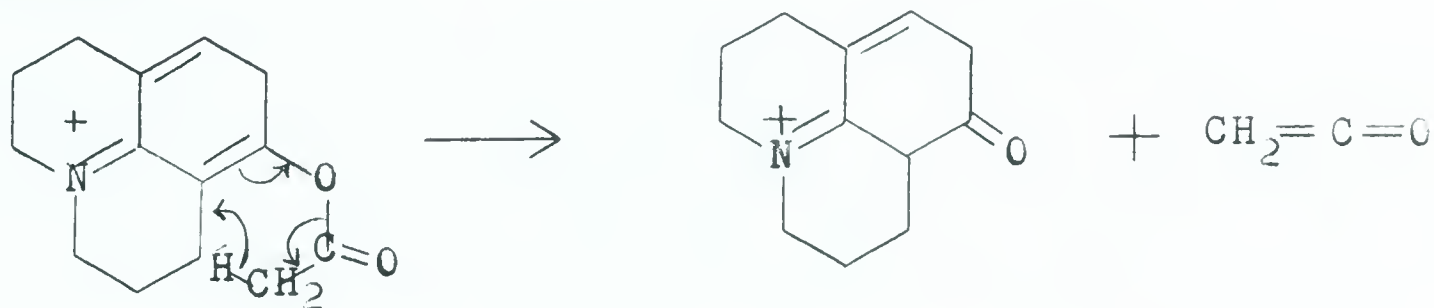
The spectrum of this alkaloid is very similar to that of

lycopodine (e.g. peaks at 190, 204, 232 and 246) and this can readily be explained by the rapid loss of ketene during ionization to give lycopodine-type fragment ions. For example the M-57 ion will have the structure:



232(12.1%)

but will be able to decompose to an ion with mass 190 by the mechanism

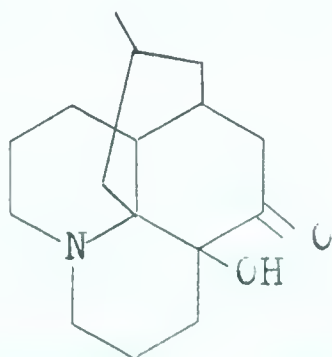


232(12.1%)

190(27.9%)

The other major peaks can be derived by loss of ketene from the "typical" ions.

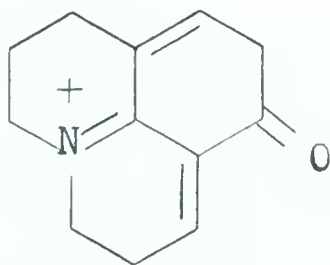
Flabelliformine



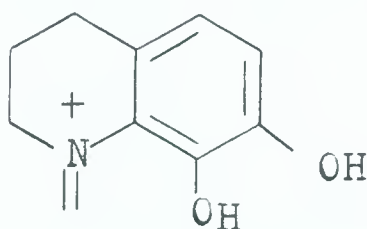
A typical fragmentation occurs to yield the larger ions, that is bridge loss followed by dehydration:



but the 188 ion will have the structure



and so cannot be expected to lose ethylene in the normal manner. The 160 peak is 1.7% of the total ionization but this may arise from loss of water from the typical ion at 178(1.1%).



This would require extensive hydrogen migration, but this seems to be a common phenomenon in reactions in the ion source (compare with 172 peak in Lycoclavine and 160 peak in 6-hydroxy-lycopodine).

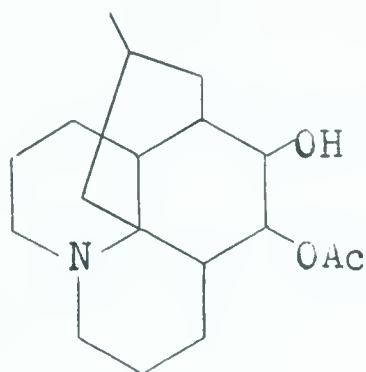
It is interesting to note that the three dihydroxy benzenes show peaks at M-18 with intensities (11)

	$\sum_{78}^{\%}$
Catechol (ortho)	3.36
Resorcinol (meta)	0.41
Hydroquinone (para)	0.23

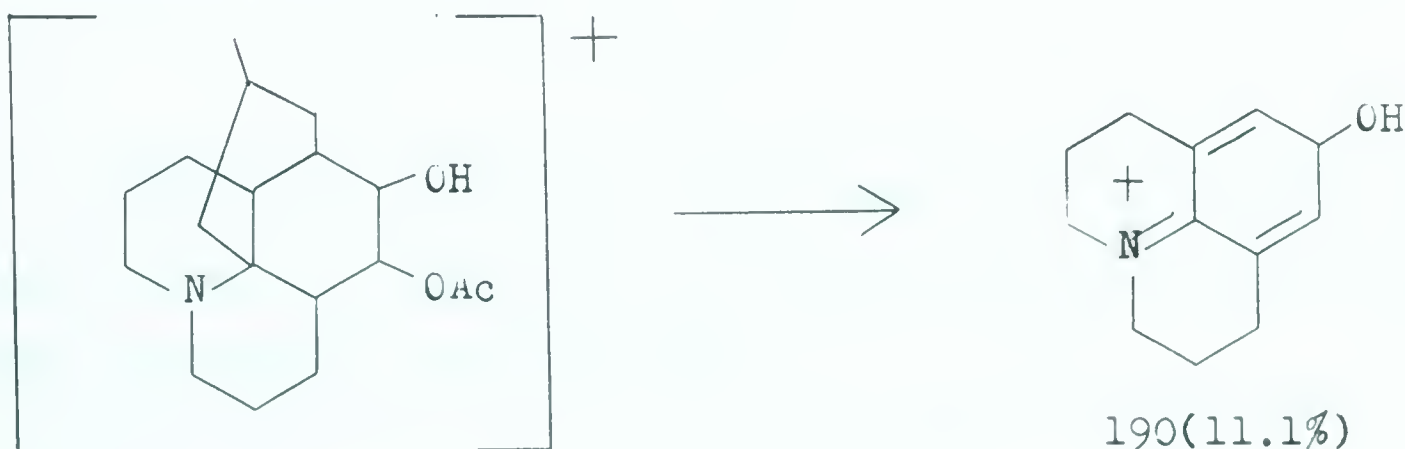
It appears then that we can expect that, whenever two hydroxyl groups are α to each other on an aromatic ring, a loss of 18 is a likely fragmentation.

Prominent peaks at 233(0.7%) and 221 (0.4%) are difficult to explain but the appearance of large peaks at 57 units less than each, viz. 176(1.1%) and 164(5.4%), indicate that these represent two further independent fragmentation patterns. It would be unwise to postulate possible structures for these ions without additional evidence and it will be safer to conclude only that a hydroxyl group on the C_4 may give rise to an anomalous fragmentation pattern.

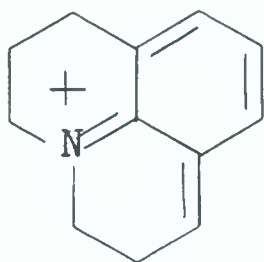
Lycoclavine



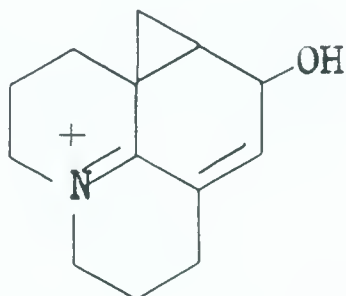
The spectrum of this alkaloid is quite typical with the exception of a prominent peak at 172. The base peak at 190 can be assumed to be due to loss of the bridge and acetic acid in the manner shown below.



Loss of water from this could explain the 172(3.7%) peak but extensive H migration would be required to give a structure such as:



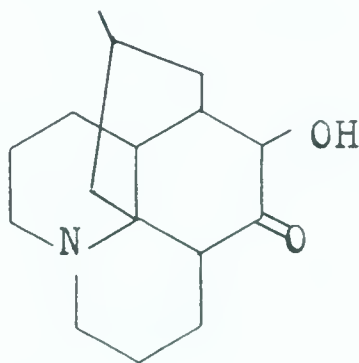
If this were the explanation then the 204 peak which is assumed to have the structure



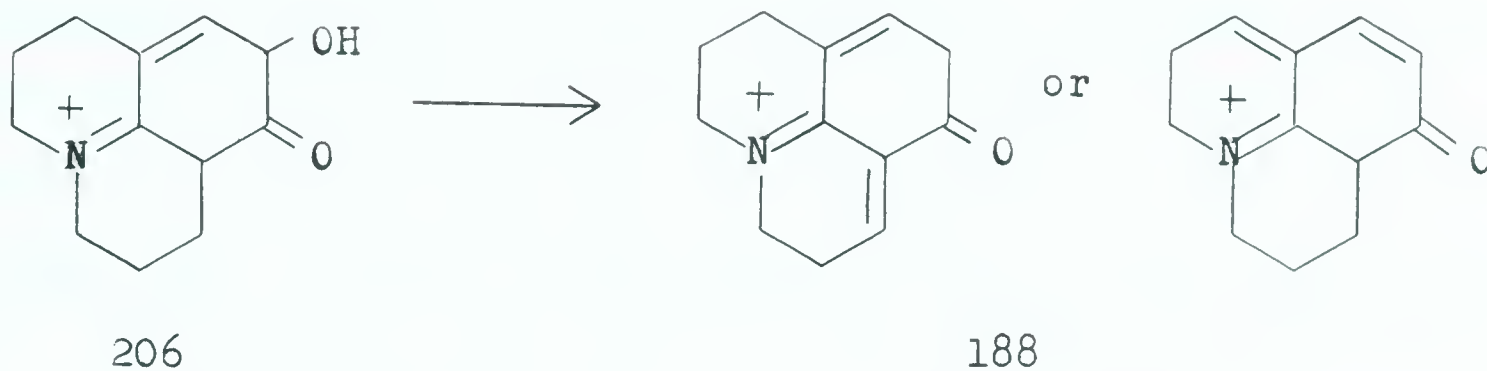
204(0.8%)

should also lose water. There is a peak at 186(0.6%) which satisfies this condition.

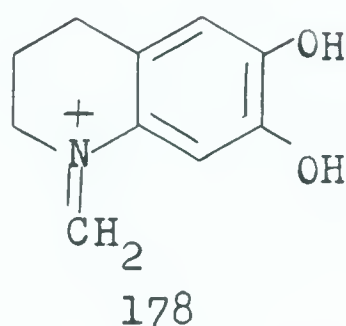
6 β -Hydroxylycopodine



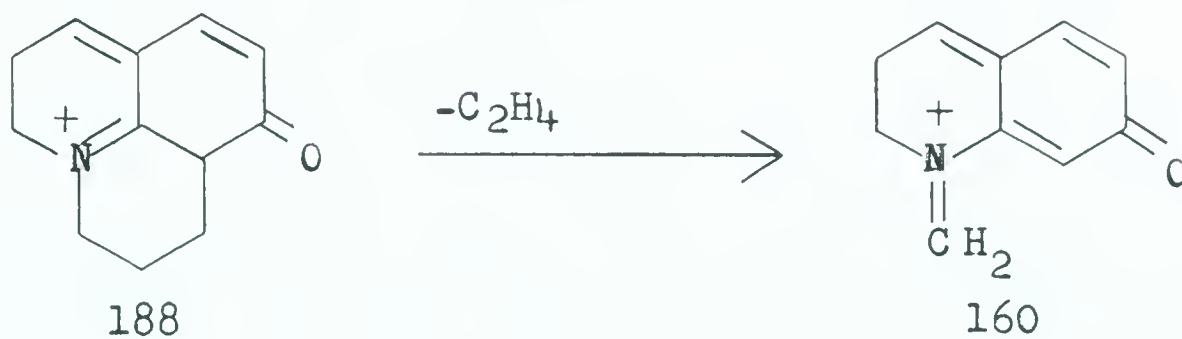
6 β -Hydroxylycopodine is very similar to lycoclavine and shows a peak at 188(2.4%) which could be due to loss of water from the typical ion 206(16.3%).



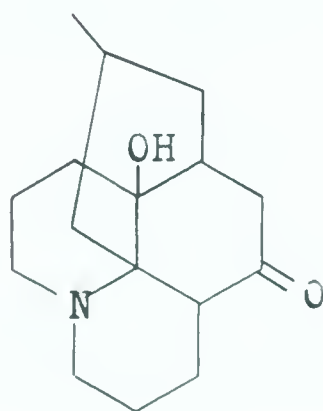
A peak at 160(1.3%) could be due to loss of water from the typical ion at 178(2.8%)



or ethylene from 188

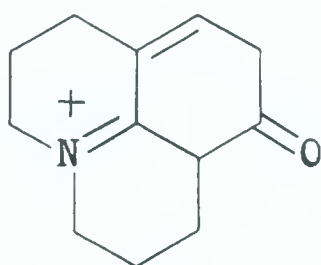


Lycodoline



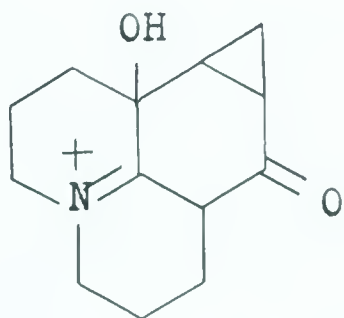
This alkaloid, as mentioned earlier, has a hydroxyl group

on C_{12} which effectively halts bridge loss, thus its spectrum is considerably different from the bulk of the alkaloids studied. It does however show the characteristic cracking pattern below 140 and so we can conclude that this "fingerprint" region is not dependant upon a typical fragmentation pattern in the higher mass range. Above 140 the most striking aspect of the spectrum is the absence of any peak which is significantly more intense than all the others. The molecular peak is the largest followed by 246(M-17) and 190. The M-17 is typical of a hydroxylated compound as mentioned earlier and the 190 could be due to the less favoured bridge and C_{12} hydroxyl loss to give the typical ion

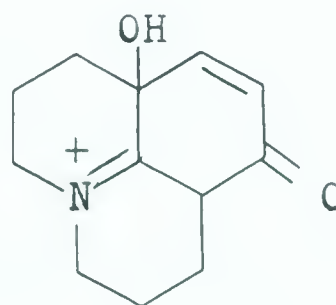


190

The intensity of this peak is only 3.4% as compared with 36.2% in lycopodine. It seems likely that the C_6 hydrogen can be eliminated in place of the typical C_{12} hydrogen in conjunction with the bridge loss to give rise to the ions



220(2.1%)

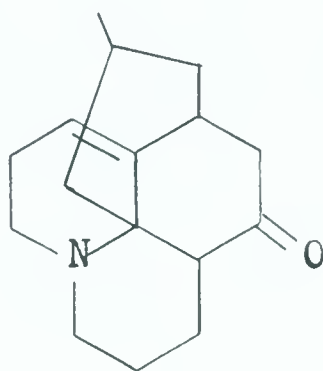


206(1.6%)

Peaks at 192(2.2%) and 178(1.9%) will be due to typical ethylene losses from each of these ions and a peak at 162(1.3%) an ethylene loss from 190.

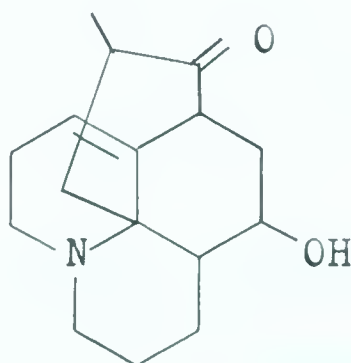
A peak at 235, M-28(1.0%) is harder to explain. The two possibilities are ethylene and CO losses from the molecular ion but any prediction of structure would be useless without further evidence (e.g. from high resolution mass spectrometry).

Anhydrolycodoline

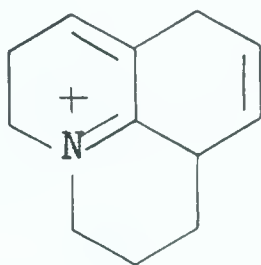


This alkaloid behaves in an exactly analogous fashion to lycodoline including a peak at M-28(0.7%). A peak at M-29(1.2%) is presumably due to loss of ethylene from the M-1 ion. This, it will be remembered, is a typical fragmentation pattern and can be observed in lycopodine and many other alkaloids. The puzzling feature is that the M-29 peak in lycodoline is only 0.2% and thus much smaller than the M-28 (1.0%).

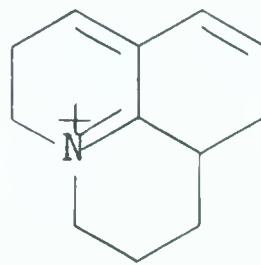
Acrifoline



Acrifoline has a spectrum which is unlike those of other alkaloids with no H on C₁₂ in that two peaks, 174(13.2%) and 191(11.6%) are very much larger than any others. Both these ions and also one at 233(4.0%) cannot be explained on the basis of any of the fragmentation patterns so far proposed. In many respects the spectrum of acrifolinol, where the carbonyl group has been reduced, is very similar to lycodoline and anhydro-lycodoline and so the unusual features of the spectrum of acrifoline appear to be associated with the carbonyl group. Acrifolinol also has its largest peak at 174 and this could be explained by either of the ions

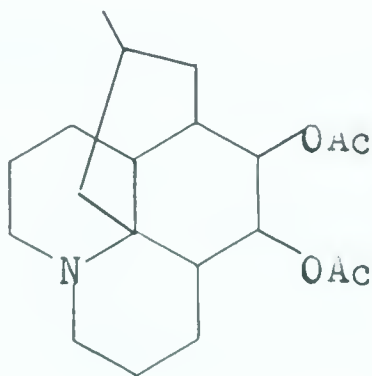


or



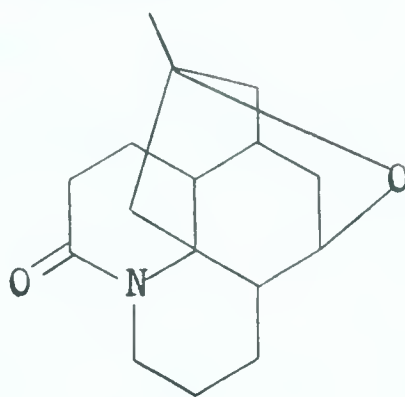
174

Lycoclavine Acetate



This does not fit into any rational pattern which may be attributable to faulty counting although no error could be found on reexamination of the original trace.

Dihydrolycopodine Lactam Ether

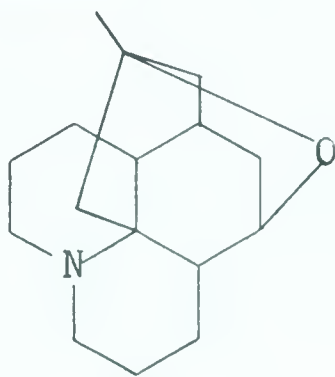


Most major peaks can be rationalized on the basis of typical fragmentation patterns, however a peak at 177(4.1%) cannot be explained. Odd numbered ions, of course, indicate either a radical ion or an ion where the nitrogen is absent. A peak at 232, presumably due to loss of C_2H_5 , is hard to explain and cannot be due to the normal pattern of loss of the hydrogen on on C_{15} together with elimination of ethylene from the C_2-C_3 position because in this alkaloid no hydrogen is present on C_{15} . A metastable peak at 135.5 could be due to the transition



and so these unexplained peaks may belong to the same alternative fragmentation series. A further large peak at 149(0.9%) is probably due to the loss of ethylene from 177(4.1%).

Dihydrolycopodine 5,15 Ether

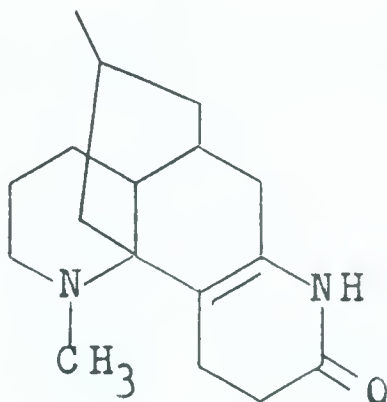


Dihydrolycopodine 5,15 ether is, as might be expected, very similar to dihydrolycopodine lactam ether except that the major peaks appear at

14 mass units lower. In particular it has a large peak at 163(5.6%) which corresponds to the 177 peak in dihydrolycopodine lactam ether. No measureable peak (i.e. $<0.1\%$) is found at M-27 but the amount of sample used for the scan was minimal and although peaks can be detected at M-27 and M-29 they are on too high a sensitivity range of the mass spectrometer to be measured with accuracy.

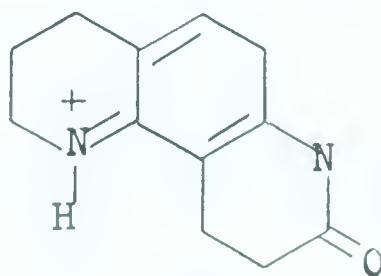
Alkaloids with Skeleta Unlike Lycopodine.

α -Obscurine



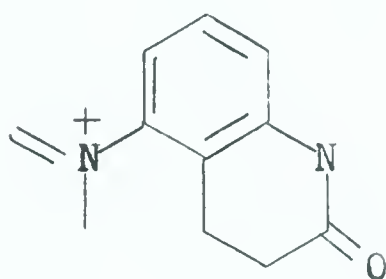
The spectrum of this alkaloid in the fingerprint region (i.e. $m/e < 150$) differs considerably from that of lycopodine and other similar alkaloids. While no other compounds with the obscurine skeleton have been studied it seems likely that they would show the same correlation with α -obscurine as do the various lycopodine-type alkaloids with lycopodine.

The major peaks indicate that the mode of fragmentation of α -obscurine is similar to that of lycopodine being dominated by bridge loss. The largest peak is at 217(25.2%) and very probably has the structure



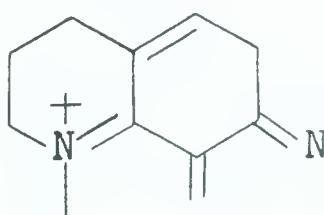
217

The other major peaks are spaced by 14, or multiples of 14, units as in lycopodine but to explain these fragments two possible modes are available. They require either the loss of ethylene from the molecule to give ions of the type



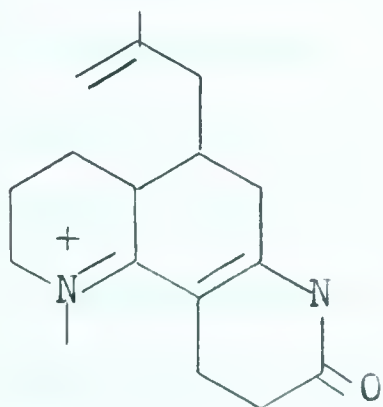
189

or loss of ketene to give ions of the type

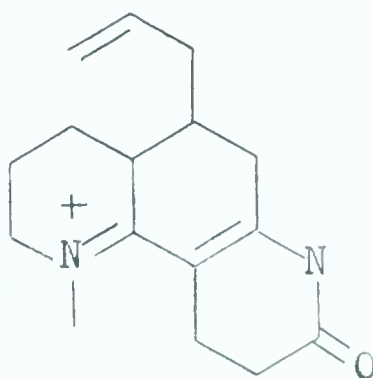


189

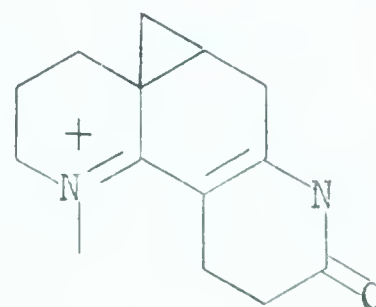
Combining either of these processes with the initial "typical" fragmentations giving rise to the ions



273(3.5%)



259(0.2%)



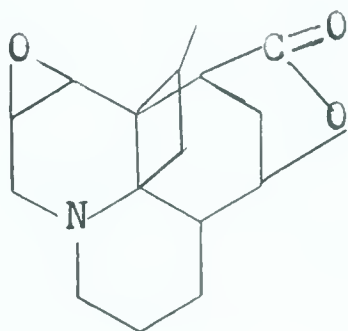
231(3.4%)

we can derive all the masses required to explain the major peaks.

The loss of ethylene requires hydrogen migration in some cases, e.g. from 217, while that of ketene requires none. A peak at 175 can only be explained by the loss of ketene but it is not large (0.5%) and perhaps is not of great significance.

If both fragmentation schemes were present we might expect peaks at 163 and 147 (these could not be obtained by any one fragmentation scheme) but both of these peaks, though present, are minor ones and are exceeded in height by 164 and 148 respectively. No definite conclusion on the structures of the fragment ions can thus be reached without recourse to high resolution mass spectrometry to show whether, for instance, the ion with mass 231 contains oxygen.

Annotinine



The region of the spectrum below $m/e = 150$ is quite similar to lycopodine. This is not unexpected because, with the exception of the bridge ring, the skeleta are similar. Above $m/e = 150$ the spectrum is quite unique and it would be unwise to attempt to characterize the peaks in this region without studying more alkaloids of the annotinine group.

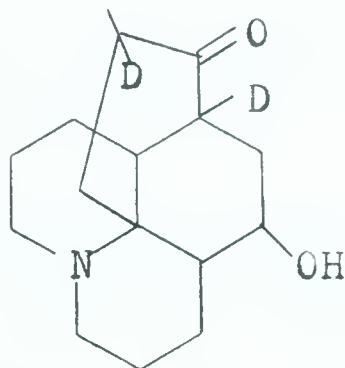
Discussion of the Results of D. B. MacLean.

While this work was being pursued, it was known that D. B. MacLean, working in the laboratories of K. Biemann, was also using mass-spectrometry to study lycopodium alkaloids. His results have since been published (12). Many of the compounds studied were common to both research programs and it will be valuable to compare these independant results particularly because the instruments used were different as also were the conditions in most cases.

MacLean used a CEC-103C mass spectrometer with a heated inlet maintained at 140°C. He also used a direct inlet method which employs a vacuum lock on the ion source for samples which appeared to decompose in the normal inlet system. He reports extensive data on metastable peaks and it seems likely that the CEC-103C gives better defined metastable peaks than the MS2-H. The electrostatically variable collector slit on the MS2-H suppresses metastable peaks and those which are detected are very diffuse and of low intensity.

In most of the spectra, those of MacLean agree well with those obtained in this laboratory and on major points of interpretation, e.g. the dominating effect of bridge loss and the ready loss of ethylene from the "B" ring, both groups are also in agreement. There are however several points of disagreement and only these will be discussed here. It should be emphasized that these are of a minor nature and mainly refer to speculative conclusions drawn from inadequate data whose limitations are well appreciated by both groups.

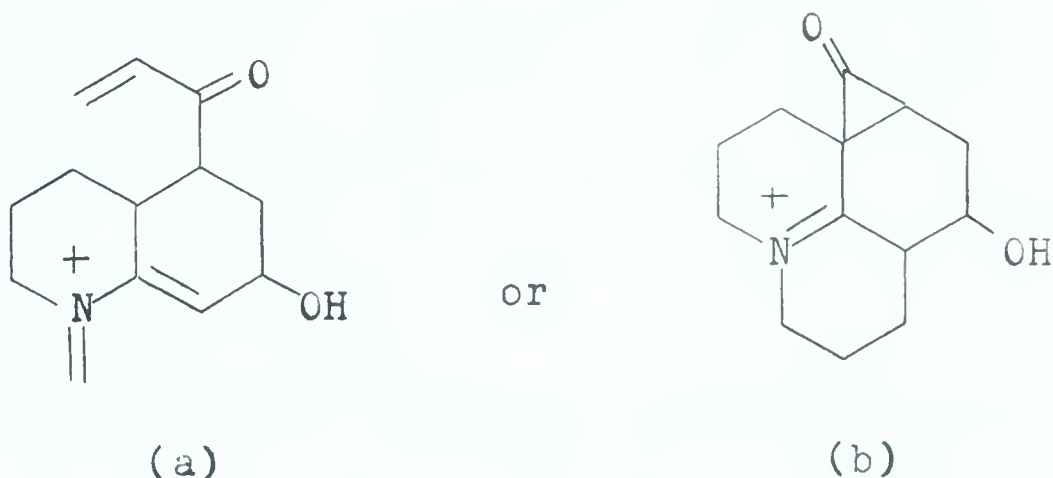
(1) MacLean reports spectra of annofoline and dideuteroannofoline (compounds which were not available to this group),



Dideuteroannofoline

and finds that the normal loss of 43 mass units from annofoline increase to 44 mass units in the deuterated compound. He concludes that "the bridge carbons are responsible for this peak in the annofoline spectrum and possibly are responsible for it, or contribute to it, in the spectra of the other alkaloids of the lycopodine group where an M-43 peak is invariably present".

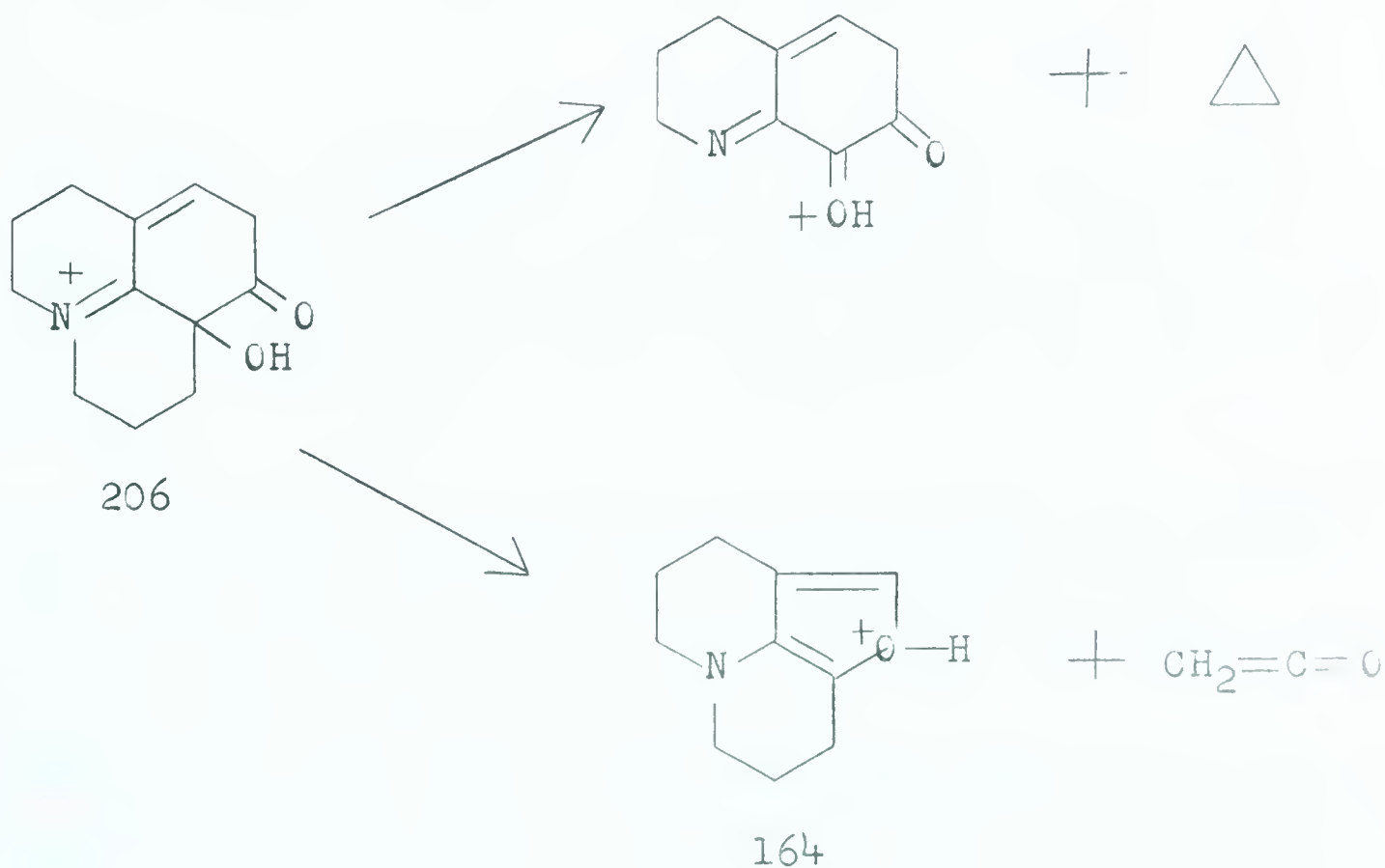
According to the fragmentation scheme we have proposed for lycopodine type alkaloids this M-43 peak should, in the case of annofoline, be due to the ions



(a) would be expected to be still M-43 in the deuterated compound while (b) would be M-44. Thus, although MacLean does not propose a structure for this ion, it appears that what he has in mind is ion (b).

No such information was derived from this study and although this does not show conclusively that ions of type (a) are not formed it does indicate that the formation of ions of type (b) is the more probable alternative.

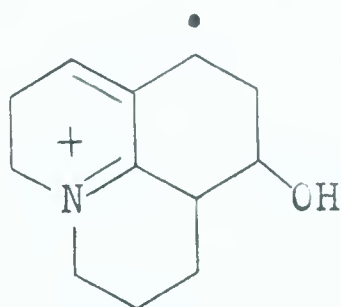
(2) The spectra of flabelliformine obtained by the two groups are very similar the main difference being that this group reports a peak at 233(0.7%). This and a peak at 221(0.4%), which both groups report but which Maclean does not discuss, are difficult to characterize. Both have peaks at 57 mass units less, 176(1.1%) and 164(5.4%), and it seems likely that these are related by loss of the bridge and hydrogen to each other. MacLean suggests two plausible structures for the 164 ion produced by loss of cyclopropane or ketene from the 206 ion



Neither could be related to the 221 peak and without supporting evidence such speculation seems of little value. It does however point out the possibility of even numbered ions having stable structures with the charge localized on an oxygen atom rather than the nitrogen.

(3) In discussing the spectrum of acrifoline, MacLean suggests that the unusual peak at 233(M-28) is due to loss of CO. Acrifolinol, which MacLean does not report, shows no peak at M-28 which supports this hypotheses.

He also suggests that the 191(M-70) peak is due to the radical ion



191

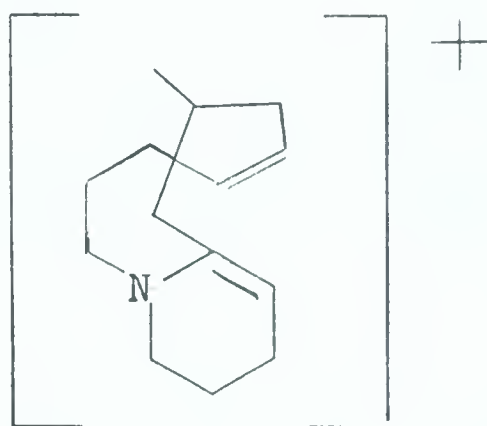
The 191 peak in acrifolinol is smaller than both the 190 and 192 peaks and there seems to be no reason why it should differ so markedly from acrifoline if this is the true structure of the 191 ion.

(4) When the spectra of lycoclavine obtained by the two groups are examined, the major differences are that Maclean finds prominent peaks at M-57(250) and M-102(205).

The absence of a 250 peak in the spectrum reported here is probably due to pyrolysis of the alkaloid in the heated inlet of the MS2-H so that AcOH is lost. A very similar situation was

found when dihydrolycopodine acetate was studied by this group. In this case the spectrum, when a direct admission system was used*, included a large peak at M-57 while in the normal inlet this was comparatively small.

The peak at 205 which MacLean finds is certainly an unexpected one and his proposed structure

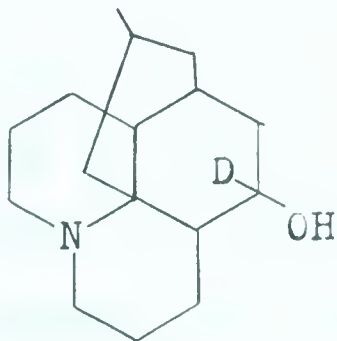


205

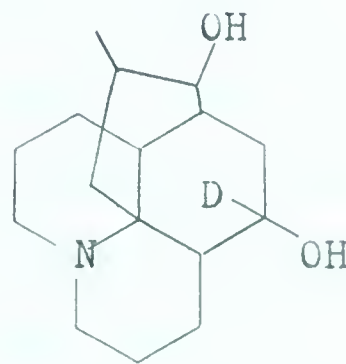
is unlike any which have been called upon to explain peaks in the spectra of similar alkaloids and one wonders whether some impurity in the sample is responsible for this.

Deuteration Studies.

Two alkaloids, 5-deuterodihydrolycopodine and 5-deuterodihydroclavolonine



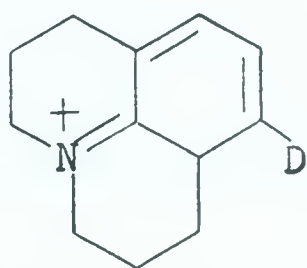
5-deuterodihydrolycopodine



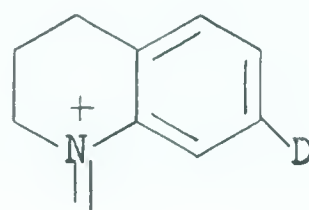
5-deuterodihydroclavolonine

* See page 246.

were prepared by the reduction of lycopodine and clavolonine with lithium aluminum deuteride. Both showed major peaks raised by one mass unit in the upper end of the spectrum, although below $m/e = 140$ they were identical with the undeuterated specimens. Peaks at 175 and 147 in the deuterated dihydrolycopodine will be due to the typical ions



175(5.4%)



147(1.9%)

and correspond to the 174(3.8%) and 146(1.9%) peaks in the undeuterated compound. However peaks at 174(4.5%) and 146(2.2%) must result from either deuterium migration and/or exchange on the walls of the inlet system* or from some alternative fragmentation pattern.

A similar effect was observed with the 5-deuterodihydroclavolonine, but also in this case a peak at 190(12.3%) which was found in undeuterated dihydroclavolonine and whose origin is obscure was unchanged (12.3%) in the deuterated compound.

One must conclude that in the present system deuteration studies are of little value probably due to exchange in the heated inlet. It should be remembered that even at low temperatures deuterium and hydrogen migration has been found to be a frequent occurrence during fragmentations in the ion source and

* MacLean found that such exchange occurred and could be prevented by pretreatment of the inlet system with MeOD.

deuterium labelling does not yield the unambiguous information that might at first be expected.

Experiments Conducted with Direct Inlet System.

Only two of the alkaloids discussed here, lycopodine and dihydrolycopodine acetate, were examined both by means of the normal heated inlet system and also using the direct inlet apparatus (Fig. 3, page 212). The spectra obtained by both methods are recorded among the mass spectra at the end of this report.

Lycopodine

When the direct inlet system was raised to about 58°C sufficient vapour pressure was obtained for an adequate scan. Comparing this spectrum with the one previously obtained at 200°C, we find that at the lower temperature all the major peaks are greater (e.g. 247(3.4%) instead of 2.3%, 190(41.7%) instead of 36.2% and 162(2.4%) instead of 1.3%) and the peaks at two mass units below major peaks are less (e.g. 188 at the low temperature is 0.5% and at the high temperature is 1.6%).

In all major respects, however, there are no noticeable differences and no difference in the interpretation of the spectrum would have been occasioned if only one of these spectra had been available. There is reason to believe that this would be the case with the great majority of the alkaloids studied, particularly those which show a substantial parent peak.

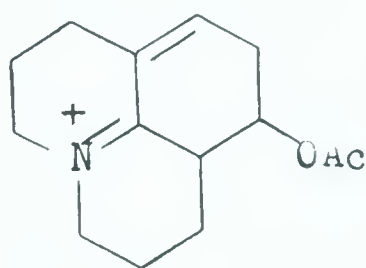
Dihydrolycopodine Acetate

This alkaloid was chosen for study using the direct inlet

system because the spectrum obtained using the heated inlet system differed noticeably from that obtained by MacLean. Also the absence of large parent peaks among the acetates was suspected to be due to pyrolysis leading to the elimination of AcOH.

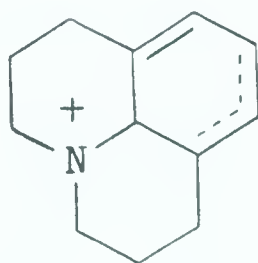
The most striking difference between the spectra obtained under the differing temperature conditions (about 70°C for the direct admission, 200°C for the heated inlet) is the appearance of 234(7.2%) as a prominent peak at the lower temperature, while at the higher temperature it was smaller (0.9%) than the neighbouring 231(2.0%) peak.

The 234 peak has the structure



234

and pyrolysis will lead to the base peak at 174 by loss of AcOH,



174

The molecular peak is also greater (0.8%) in the direct inlet spectrum than in the heated inlet spectrum (0.2%).

While the differences between the two spectra are quite

noticeable it is doubtful whether such differences could ever confuse the interpretation of a spectrum of this kind.

It seems safe to conclude that the effects of pyrolysis on the mass spectra of lycopodine-type alkaloids lead to peaks which are already prominent in the spectrum of the unpyrolysed alkaloid and so do not seriously compromise the use of mass-spectrometry in the elucidation of molecular structure. While it would be desirable to catalogue spectra obtained at the lowest possible temperatures for reference purposes this would not be of much practical value. The only reason for using such definitive spectra would be for identification of an alkaloid by showing that it has a mass spectrum which is identical with that of a known alkaloid. The mass spectrometer, however, does not adequately distinguish between stereoisomers and so only extreme paucity of sample could warrant its use in this way. Only spectra obtained under identical conditions in the same instrument can be expected to be exactly superimposable.

Metastable Peak Data.

As has been mentioned earlier, the MS2-H mass spectrometer tends to suppress metastable peaks and when these do occur they are diffuse, of very low intensity and usually lie somewhat above (approximately 0.4 mass units) the values calculated.

In Table I (page 249), the identifiable metastable peaks found in this investigation are listed together with their deviations from the calculated m/e values.

The most outstanding feature of these data is that the

TABLE I

METASTABLE PEAK DATA

Compound	m* expt.	m*calc.	Deviation	Transition	Loss
Lycopodine	146.5	146.2	+0.3	247 → 190 + 57	Bridge Ethylene
	138.0	138.2	-0.2	190 → 162 + 28	
Epilycopodine	146.5	146.1	+0.4	247 → 174 + 73	Bridge Ethylene
	138.0	138.1	-0.1	190 → 162 + 28	
Dihydrolycopodine	122.8	121.7	+1.1	249 → 174 + 75	Bridge + H ₂ O Bridge
	148 (?)	148	0	249 → 192 + 57	
Anhydrodihydrolycopodine	131.5	131.1	+0.4	231 → 174 + 57	Bridge Ethylene
	122.8	122.3	+0.5	174 → 146 + 28	
Clavolonine	136.5(?)	137.1	-0.6	263 → 190 + 73	Bridge
Dihydroclavolonine	122.8	122.4	+0.4	174 → 146 + 28	Ethylene Ethylene
	138 (?)	138	0	190 → 162 + 28	
Clavine ketol	161.5	161.3	+0.2	263 → 206 + 57	Bridge Ethylene
	153.5	153.8	-0.3	206 → 178 + 28	
Flabelliformine	136.5	134.5	+2.0	263 → 188 + 75	Bridge + H ₂ O
α-Lofoline	122.8	122.4	+0.4	174 → 146 + 28	Ethylene AcOH
	129.8(?)	129.4	+0.4	234 → 174 + 60	
Fawcettine	123	122.4	+0.6	174 → 146 + 28	Ethylene
Lycoclavine	138.5	138	+0.5	190 → 162 + 28	Ethylene
Dihydrolycopodine acetate	122.8	122.4	+0.4	174 → 146 + 28	Ethylene Bridge
	131.5	131.2	+0.3	231 → 174 + 57	

TABLE I - Continued

Compound	m*expt.	m*calc.	Deviation	Transition	Loss
Lycopdoin enol acetate	138.2 186.8(?)	138 186.1	+0.2 +0.7	190 → 162 + 28 289 → 232 + 57	Ethylene Bridge
α-Obcurine	172.5 165	172 164.6	+0.5 +0.4	274 → 217 + 57 217 → 189 + 28	Bridge Ethylene(?)
Dihydrolycopodine 5,15 ether	123.0	122.5	+0.5	247 → 174 + 73	Bridge
Δ ^{8,15} -dehydrodihydro- lycopodine	122.8	122.5	+0.3	247 → 174 + 73	Bridge + H ₂ O

Average deviation = +0.4

transitions resulting in metastable peaks are almost solely due to loss of the bridge ring and hydrogen or loss of ethylene. The only exceptions involve loss of AcOH or loss of H₂O in addition to bridge loss.

Thus it can be seen that no extensive information can be derived from interpretation of metastable peaks although it does point out the generality of bridge and ethylene losses in this series of alkaloids.

Alkaloids of Unknown Structure.

A number of alkaloids whose structure was unknown but which might be related to the alkaloids which are reported here were also examined mass-spectrometrically and an attempt was made to elucidate their structure by comparison with the spectra of the known alkaloids.

This procedure met with varying degrees of success but it is safe to say that in all cases some new information regarding their structure was obtained while in a few cases a complete structure could be proposed with reasonable certainty. We will discuss each of these alkaloids individually.

Diol from Lycopodium Clavatum var. Megastachon.

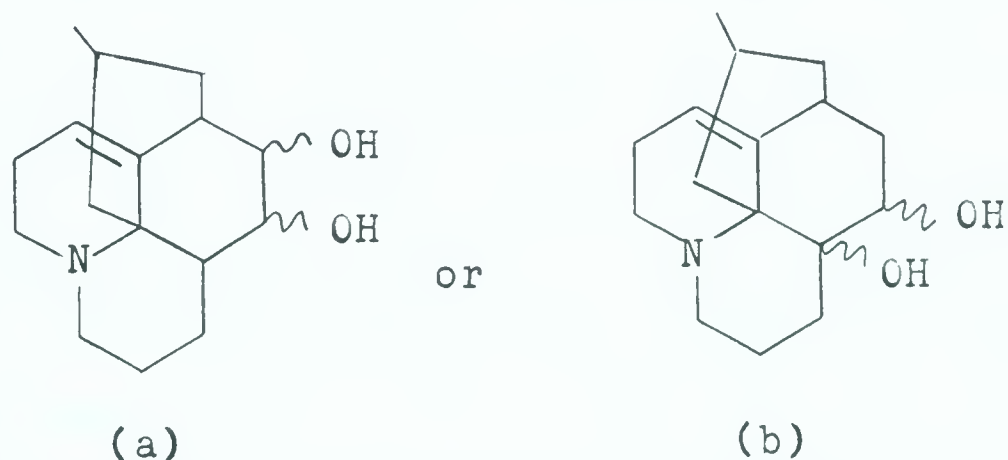
This alkaloid had been isolated by D. A. Law and conventional analytical techniques had shown that it contained one or more hydroxyl groups, no carbonyl group and probably had the molecular formula C₁₆H₂₅₋₂₇O₂N. Only a very small amount of

material was available and this coupled with its insoluble nature made it impossible to obtain a useful N.M.R. spectrum.

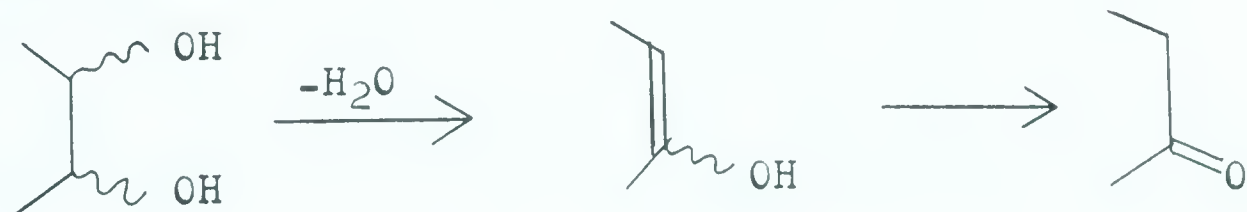
The mass spectrum showed that:

- i. The molecular weight is 263 indicating a molecular formula of $C_{16}H_{25}O_2N$.
- ii. The spectrum in the region $m/e < 150$ is typically lycopodine-like and so the basic skeleton is probably closely related to lycopodine.
- iii. Peaks are present at M-17, M-18 and M-19 indicating the presence of at least one hydroxyl group.
- iv. Below $m/e \sim 204$ the mass spectrum is virtually identical to that of anhydrolycodoline.

These results are consistent with the alkaloid being a diol with a double bond in the $C_{11}-C_{12}$ position with the structure



It will be seen that loss of water from (a) would give anhydrolycodoline



and a close similarity in mass spectra with anhydrolycodoline would be expected. (Such a similarity exists between lycopodine

and desacetyllycoclavine.) A synthesis of 11,12 dehydrides-acetyllycoclavine for comparison seems justified but lack of sufficient quantities of anhydrolycodoline or lycodoline have prevented this at the present time.

Alkaloid L-9

In 1943 Manske and Marion reported (14) the isolation of a basic substance, M.P. 122°C, from Lycopodium Annotinium L. which they designated "Alkaloid L-9". At that time they stated that "Alkaloid L-9 is probably a mixture but, owing to its exceptional behaviour, it has been deemed advisable to retain one designation only until more can be ascertained concerning its nature." Through the courtesy of R. H. Manske a sample of Alkaloid L-9 was obtained by this group.

Thin layer chromatography (t.l.c.) over alumina revealed the presence of at least two components, one having the same R_f value as lycopodine and the other having a lower R_f value.

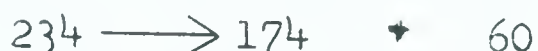
The mass spectrum showed all the characteristic peaks of lycopodine, indicating that this is, indeed, one component, together with weak peaks at 349, 290 and 289 and moderately intense peaks at 234 and 174. The peak at 349 must be the parent of the other component and a peak at 60 indicated that an -OAc group was present. Peaks at 290(M-59) and 289(M-60) are further verification of this (I.R. spectroscopy also indicated an -OAc group).

When the contribution from lycopodine (assuming that the 190 peak is all due to lycopodine) is subtracted, the peaks at 234 and 174 are the most intense peaks of the residuum and these are consistent with a component of M.W.=349 with a lycopodine-type

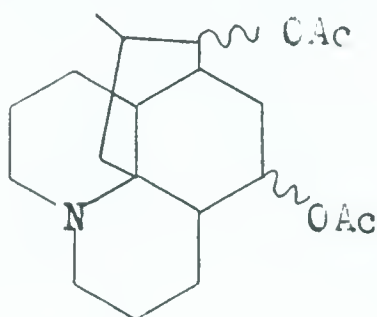
skeleton losing a bridge, which carries an -OAc group, together with hydrogen.



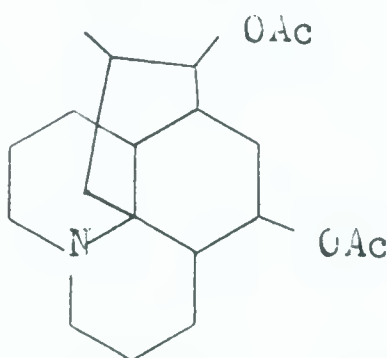
and then this typical ion losing AcOH



A structure which would account for this would be



It was thought that the naturally occurring O-acetylfawcettiine



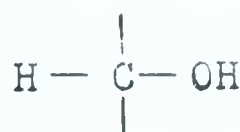
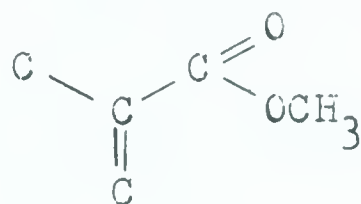
might be the unknown component but when a mixture of this and Alkaloid L-9 was subjected to t.l.c., three distinct spots were obtained.

The C₈ epimer of O-acetylfawcettiine, O-acetylloline, prepared by acetylation of loline was, however, indistinguishable by t.l.c. from the lower R_f component of Alkaloid L-9. The mass spectrum of O-acetylloline showed the expected peaks, the base peak appearing at 174(17.3%). Crystallization of a 1:1 mixture of lycopodine and O-acetylloline from hexane yielded crystals M.P. 121-122°C identical (mixed M.P., infrared spectrum, t.l.c. behaviour) to authentic Alkaloid L-9 which is thus a

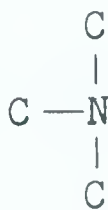
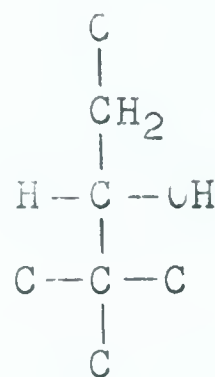
molecular complex of the two substances.

Annopodine

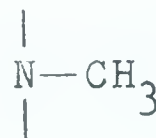
This alkaloid has been isolated by Iverach and Ayer from *L. annotinium* and preliminary investigation (15) has indicated a molecular formula of $C_{17}H_{25}O_3N$ (M.W. = 291) and the following functional groups have been shown to be present



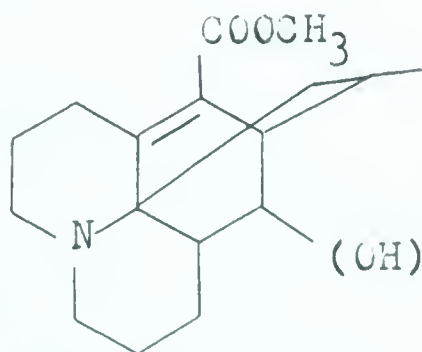
perhaps



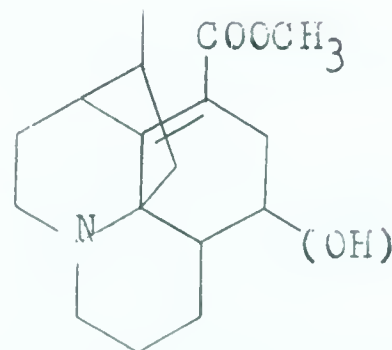
but not



Tentative structures proposed are



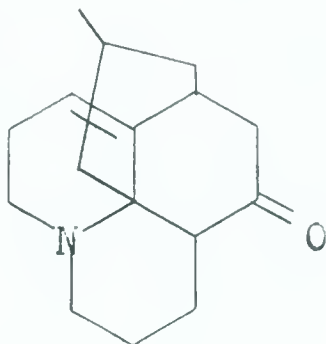
A



B

The mass spectrum of annopodine shows that the molecular weight is 291, and the region below $m/e = 150$ is of the lyco-

podine type. Of the alkaloids studied, the one whose mass spectrum it most resembles is anhydrolycodoline



anhydrolycodoline (M.W. = 245)

Below $m/e = 160$, the spectra are virtually identical with the exception of a smaller peak at 43 and a larger peak at 59 in annopodine. The 59 peak, as mentioned earlier, is indicative of a methyl ester grouping being due to the ion $[COOCH_3]^+$.

Above $m/e = 160$ annopodine differs in several respects from anhydrolycodoline. The 248(M-43) base peak is 16.9% of the total ionization while in anhydrolycodoline the 202(M-43) peak has exactly the same intensity as the parent, 9.4%, both being larger than any other peak in the spectrum.

If we examine the other major peaks in the annopodine spectrum we find:

- (a) 276, M-15 (1.6%) This will be due to loss of $-CH_3$ and is common to anhydrolycodoline (1.6%) and many other lycopodine-type alkaloids.
- (b) 274, M-17 (0.9%) This might be indicative of $-OH$ loss but it has been found that all hydroxyl-bearing alkaloids studied also give prominent peaks at M-18 and M-19. There are no such significant peaks in annopodine.
- (c) 260, M-31 (9.1%) This is no doubt due to the loss of $-OCH_3$

and is a common loss among methyl esters.

(d) 234, M-57 (3.8%) This will be due to loss of C_4H_9 and is paralleled by the 188, M-57 (3.9%) peak in anhydrolycodoline.

(e) 216, M-75 (2.7%) This may be due to loss of water from the 234 peak. There is no corresponding M-75 peak in anhydrolycodoline; which agrees with this hypothesis.

(f) Peaks at 188(2.1%) and 190(2.1%). Anhydrolycodoline has a peak at 188(3.9%) and a minor one at 190(0.9%).

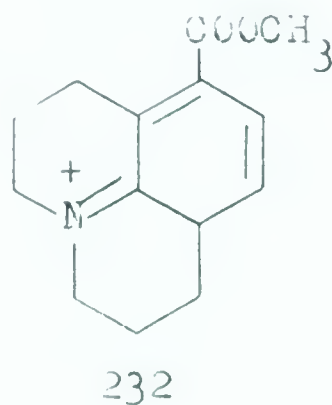
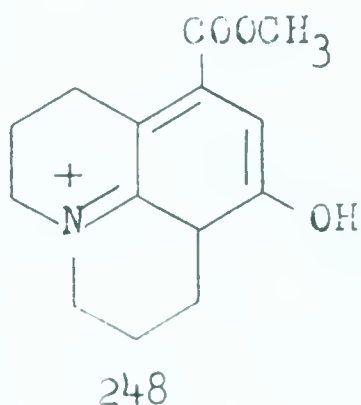
Anhydrolycodoline, like many other lycopodine-type alkaloids, shows peaks 28 mass units less than the major peaks due to loss of ethylene from ring B e.g. at M-29 (M-1-28), M-71 (M-43-28) and M-85 (M-57-28). Annopodine has no significant peaks at these masses.

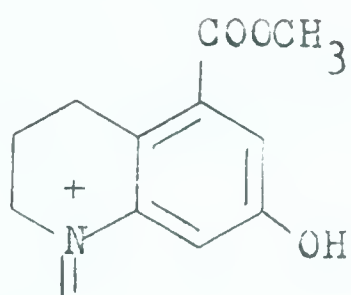
If we now consider the two tentative structures and attempt to predict the salient features of their mass spectra we might expect that

(i) Neither spectrum need resemble that of anhydrolycodoline closely.

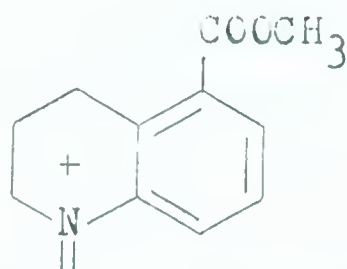
(ii) Both should give the characteristic peaks of hydroxylated alkaloids (M-17, M-18, M-19) and 18 mass unit "gaps" in the spectrum.

(iii) A might be expected to give the ions



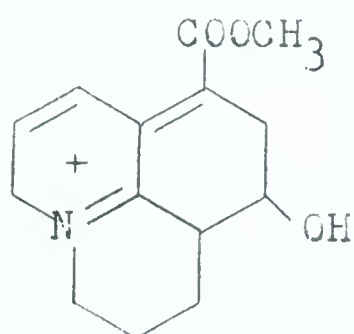


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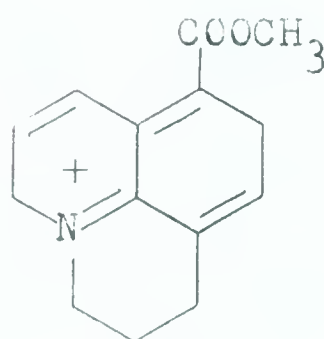


204

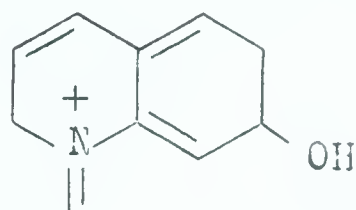
B might be expected to give the ions



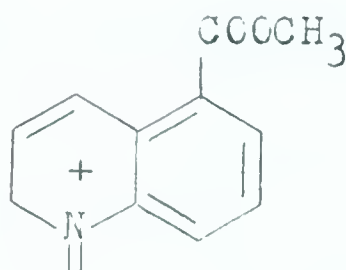
248



230



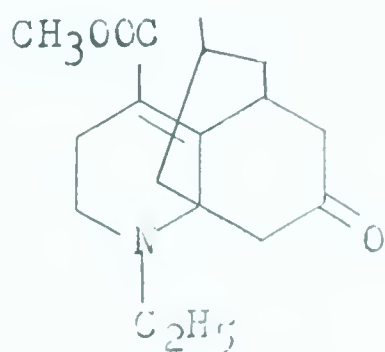
220



202

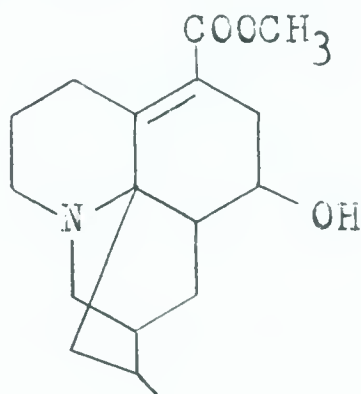
It will be seen that only the 248 peak agrees with the observed spectrum.

If one were to postulate a structure on the basis of the mass spectrum alone it would probably be of the type



This, of course, is in conflict with the chemical evidence for the structure in several major respects which points out the danger of putting too much reliance on mass spectral evidence alone.

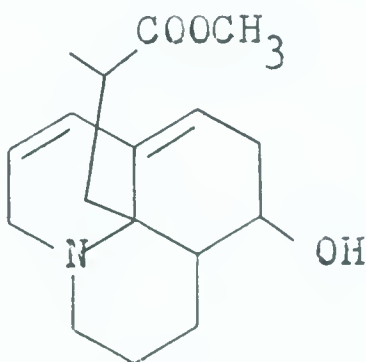
A structure which would fit the chemical evidence and also agree more closely with the observed mass spectrum is



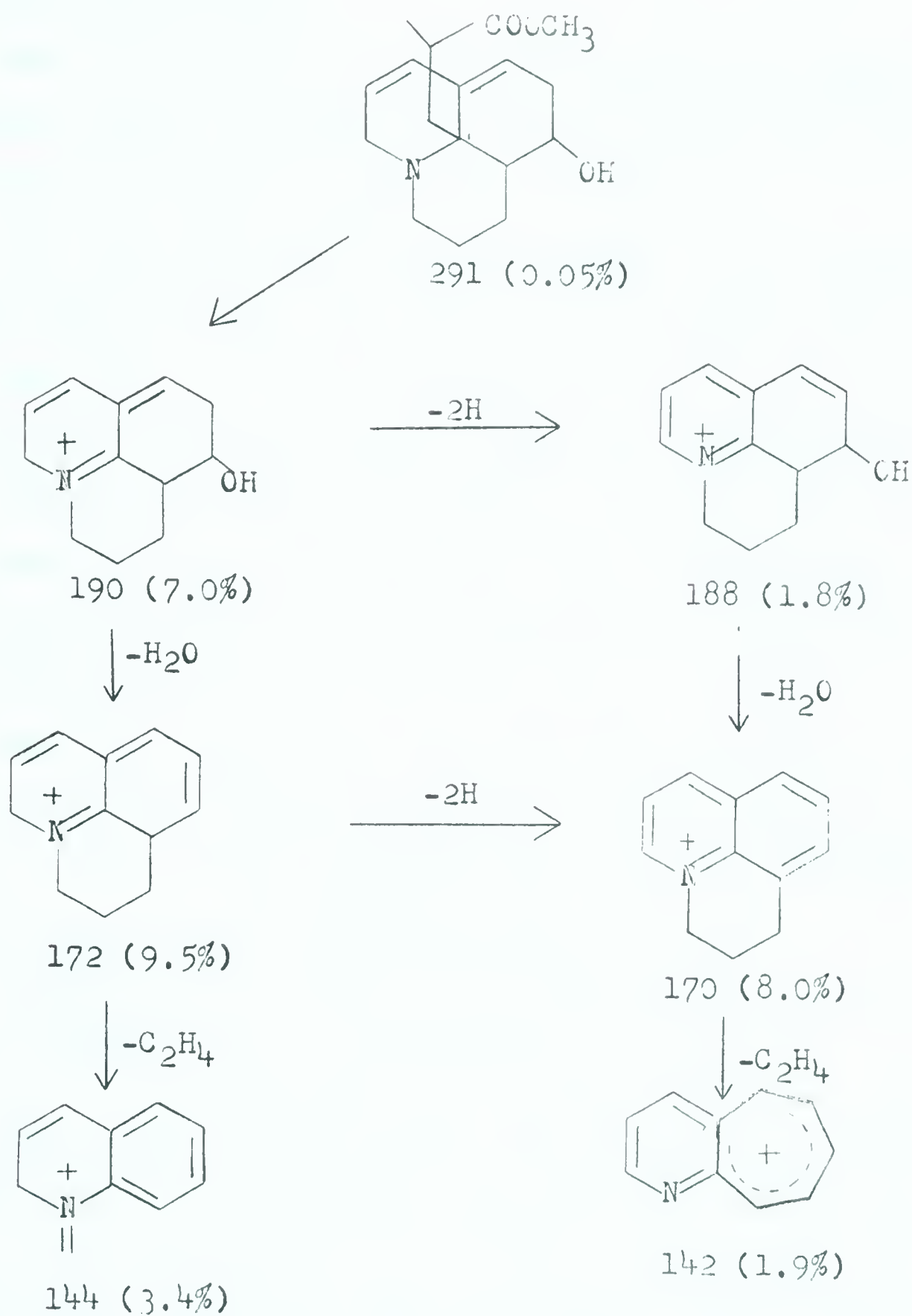
however this does not explain the M-57 peak and the absence of characteristic -OH dependant peaks.

Lyconnotine

Very recently (16) a structure has been suggested for this alkaloid. This is



The mass spectrum verifies the molecular formula $C_{17}H_{25}O_3N$ (M.W. = 291) and the major peaks observed can be rationalized by the following fragmentation scheme.



In this instance it appears that mass spectrometry supplies valuable corroborating evidence for a structure which was arrived at mainly on the basis of NMR data.

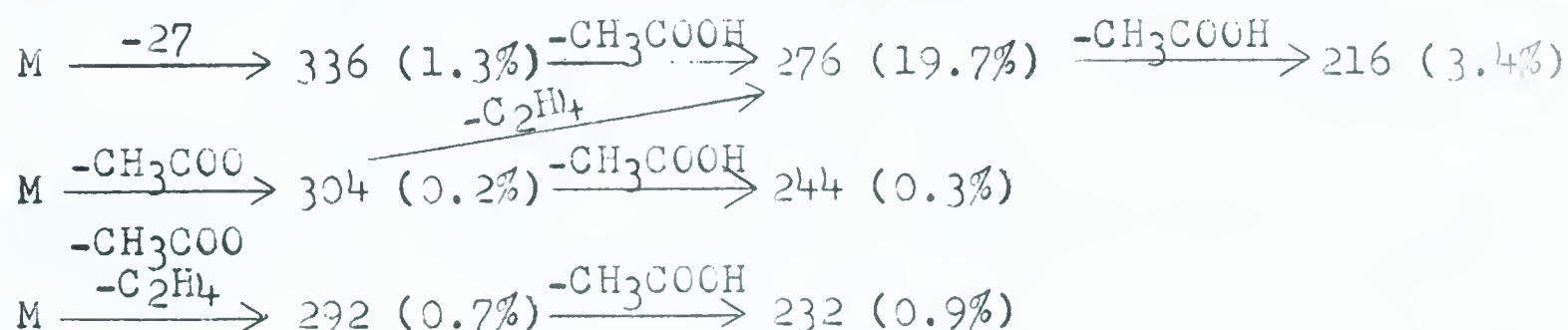
Diacetyl Serratinine

This uncharacterized alkaloid (supplied by Inubushi et al (18)) was thought to contain two acetate groups and have the molecular formula $C_{20}H_{29}O_5N$ (M.W. = 363).

The mass spectrum shows what appears to be a parent peak at 363 which is small but this is to be expected with acetates (see page 226). A peak at 304 (M-59) is also observed which reinforces this conclusion. A peak at 60 indicates an acetate.

The spectrum below $m/e = 150$ is not very similar to those of lycopodine-type alkaloids, but those alkaloids studied which most closely resemble it are clavine ketol, lycoclavine acetate, and deacetyllycoclavine.

The major peaks above $m/e = 150$ are difficult to characterize but at least three fragmentation series appear to exist.



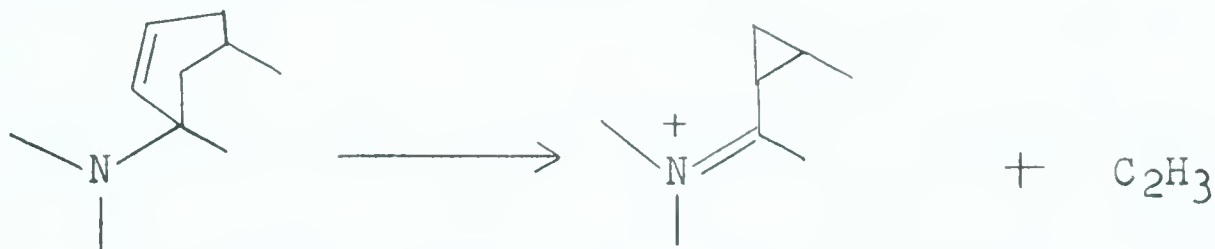
Major peaks at 322 (0.1%), 260 (0.3%), 194 (5.0%) and 152 (7.2%) do not fit readily into any of these schemes nor do they form a credible fragmentation series in themselves. The only identifiable metastable peaks are at $m/e = 228$ and 169.5 and must be due to the transitions.



A puzzling feature of the spectrum is the 336 (M-27) peak. The only plausible fragments which could account for 27 mass

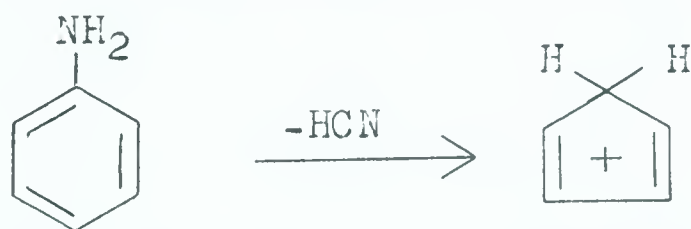
units are C_2H_3 and HCN.

C_2H_3 , by analogy with the lycopodine-type alkaloids, might be favourably lost in the situation

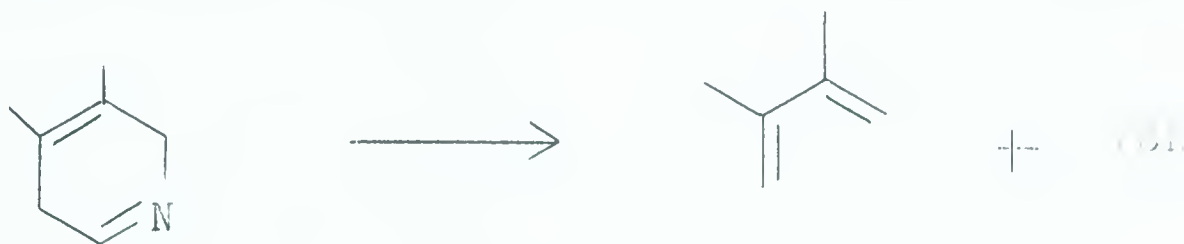


The loss of HCN has not been noted in any compounds in this investigation and it might be expected that such an initial loss might lead to odd-numbered ions. All the major peaks, however, are even-numbered, indicating that the N is still probably present.

It should be remembered that HCN is usually the most favoured loss from primary aromatic amines. e.g.



One could also conceive that an elimination of HCN of the type



might occur if a suitable structure existed in the molecule.

Cernuine and Lycocernuine

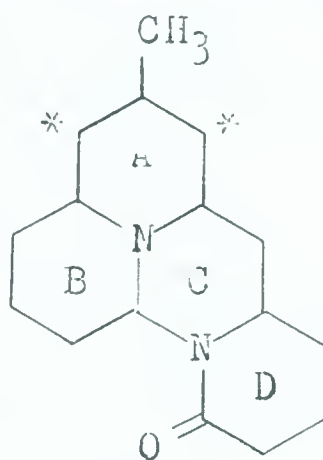
These two alkaloids of unknown structure give mass spectra which are considerably different from those already studied. The molecular weights found agree with the tentative molecular

formulae i.e.

Cernuine	$C_{16}H_{26}ON_2$	M.W. = 262
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Lycocernuine	$C_{16}H_{26}O_2N_2$	M.W. = 278
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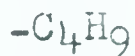
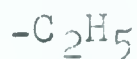
Recent chemical work coupled with biogenetic speculation, suggests that cernuine may have structure I, lycocernuine differing only in that it has a hydroxyl at one of the starred positions.



I

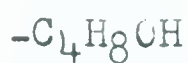
When these alkaloids are examined mass-spectrometrically we find that the two spectra are similar except that lycocernuine shows peaks typical of a hydroxylated compound i.e. peaks at M-17 and M-19 (M-18 is very small).

The major peaks in cernuine correspond to the losses



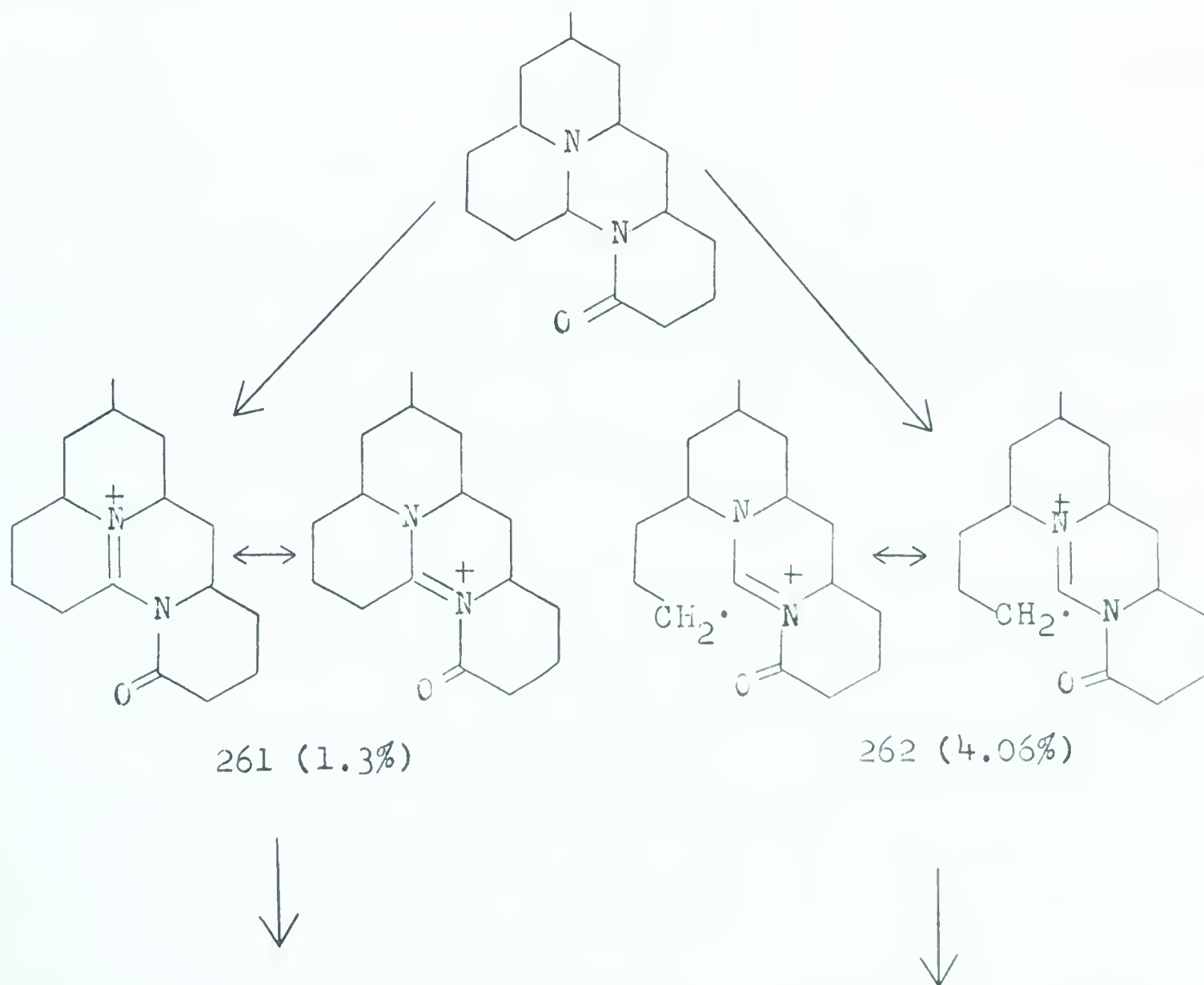
while in lycocernuine peaks corresponding to losses of the two series

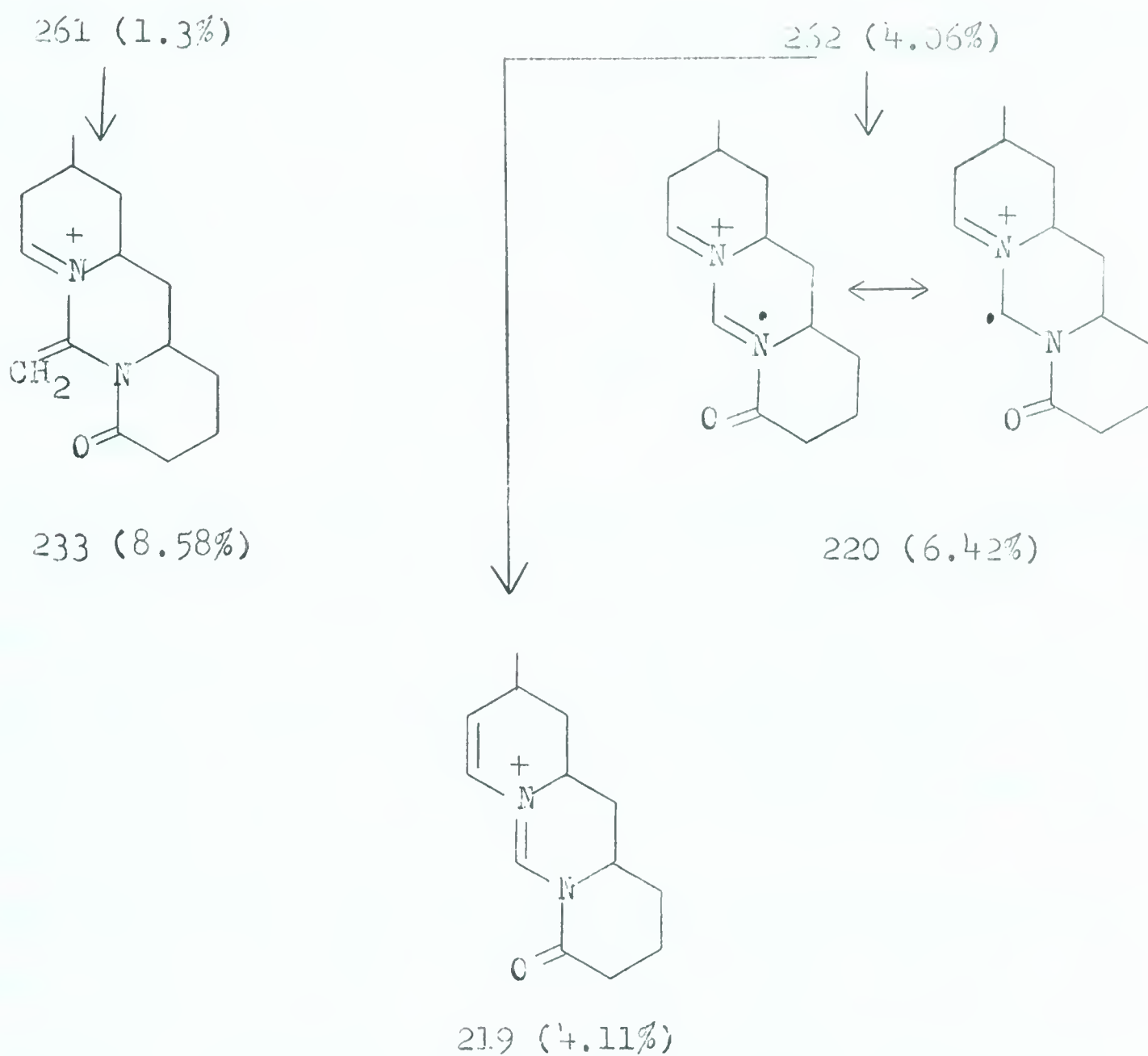




are observed.

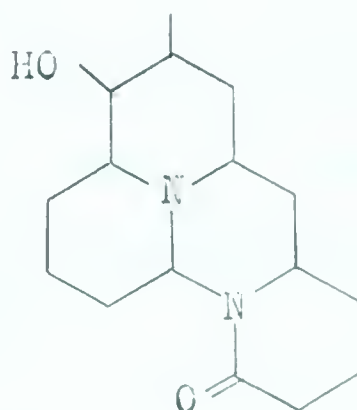
When we attempt to predict how structure I might fragment we find that there is no tertiary carbon atom α to a nitrogen atom as in the lycopodine-type alkaloids and so such a favoured bond cleavage leaving the ionic charge localized on the nitrogen is impossible. However if either a C—C or a C—H bond on the C atom which is α to both nitrogens were to cleave, the resulting ion would be stabilized by resonance. Assuming that this is the initial cleavage, we can postulate a plausible fragmentation scheme for cernuine which accounts for all the major peaks.



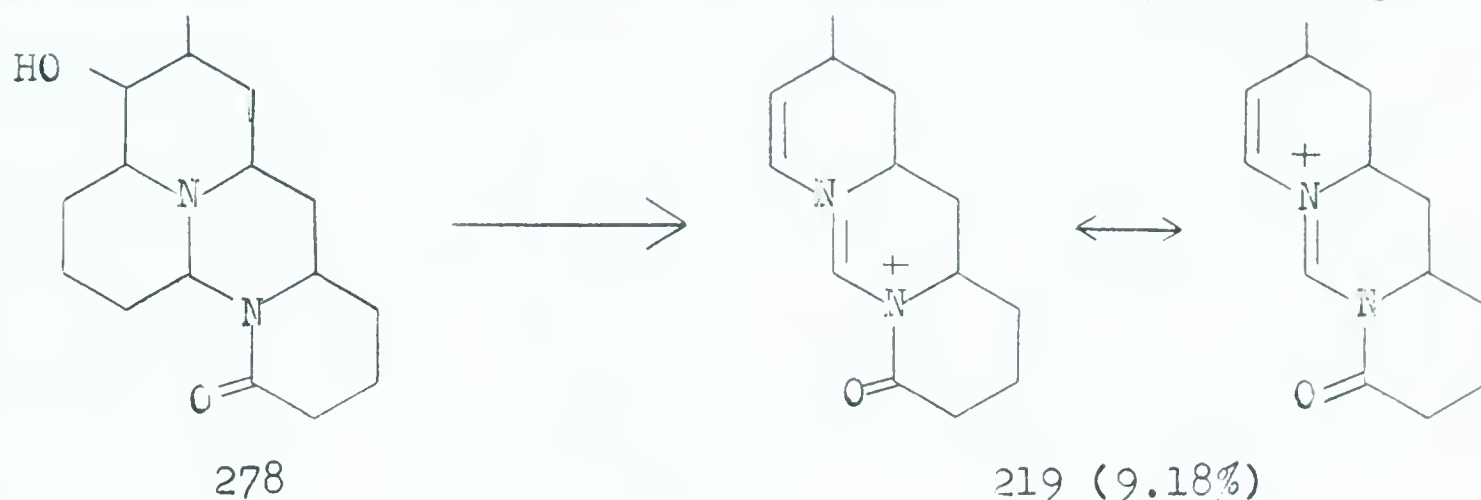


The stability of the 220 ion, which gives rise to a major (6.42%) peak, is rendered understandable by this explanation.

If this basic fragmentation pattern is extended to lycocernuine we require the structure



so that the base peak at 219 can be explained by the fragmentation



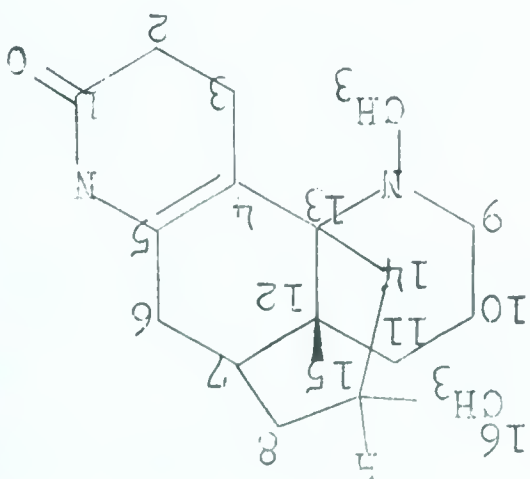
This does not explain the large (5.57%) peak at 220 and one wonders whether the 219 and 220 peaks which appear in both cernuine and lycocernuine have the same structure. If this were the case then it would require that the hydroxyl group in lycocernuine be on ring B. N.M.R. studies, however, indicate that it is β to the methyl group.

Mass spectra of dihydrodeoxycernuine and dihydrodeoxylycercernuine, where the carbonyl functions in these alkaloids have been reduced to methylene groups, are related to each other in exactly the same way as the parent compounds. This indicates that the carbonyl function has no effect on the basic fragmentation pattern. (A similar situation is found with lycopodine and lycopodane.)

Sauroxine

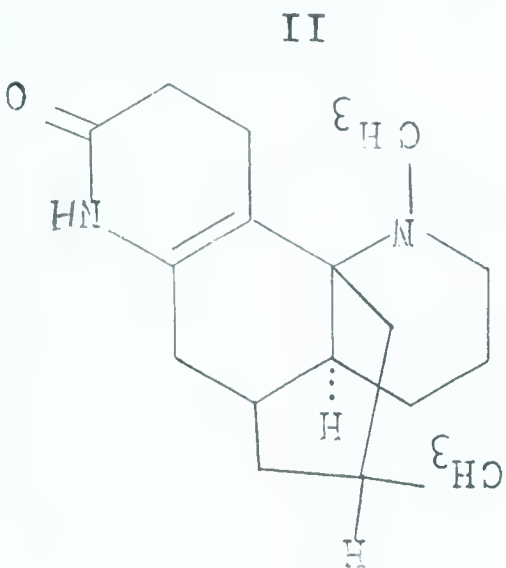
The mass spectrum of this alkaloid is very similar to that of α -obscurine. All the major peaks in both spectra occur at the same m/e values but there are some significant intensity differences. It appears extremely probable that these two alkaloids are stereoisomers.

The stereochemistry of α -obscurine is shown below I (13)



I

α -Obscurine contains 4 asymmetric carbons (C-7, C-12, C-13 and C-15) but the fusion of the bridge at C-7 and C-13 fixes the configuration at these two centres. If sauroxine is a stereoisomer of α -obscurine it must differ only at C-12 and C-15. N.M.R. measurements indicate that a different configuration at C-15 is unlikely hence structure II is indicated.



II

This means that sauroxine bears the same relationship to α -obscurine as epilyclopodine does to lycopodine. In Table 2

the ratios of corresponding ion intensities in epilycopodine and lycopodine and sauroxine and α -obscurine are listed.

TABLE 2

Ion	Epilycopodine	Sauroxine
	Lycopodine	α -Obscurine
M	1.17	0.82
M-15	4.78	2.17
M-29	2.93	1.50
M-43	4.03	1.27
M-57	0.57	0.57
M-71	3.18	1.67
M-85	3.46	0.98

While there is no very close similarity between the ratios they do in general follow similar trends, e.g. the base peak (M-57) in both cases is reduced in the "epi" isomer by nearly one-half.

The two pairs of alkaloids have basically different structures and so a closer agreement between the ratios in Table 2 could not be expected.

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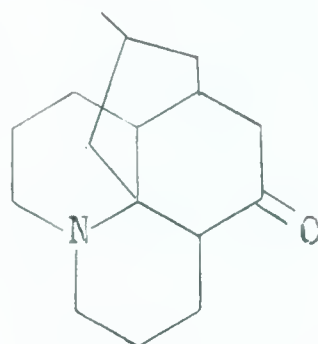
Lycopodine

$C_{16}H_{25}ON$

M.W. 247

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.10	97	0.16	177	0.17		
27	1.45	103	0.15	178	0.08		
28	2.40	104	0.15	184	0.08		
29	1.38	105	0.48	185	0.03		
30	0.55	106	0.56	186	0.47		
39	1.48	107	0.35	187	0.09		
40	0.36	108	0.49	188	1.62		
41	3.85	109	0.15	189	0.38		
42	1.62	110	0.13	190	36.20		
43	1.10	115	0.12	191	4.86		
44	1.23	116	0.08	202	0.18		
51	0.22	117	0.30	204	0.79		
52	0.27	118	0.29	205	0.23		
53	1.25	119	0.26	216	0.05		
54	0.98	120	0.78	217	0.04		
55	1.39	121	0.34	218	0.15		
56	0.58	122	0.52	219	0.06		
57	0.15	123	0.31	230	0.07		
65	0.63	130	0.19	232	0.18		
66	0.32	131	0.17	244	0.68		
67	1.09	132	0.48	245	0.59		
68	0.60	133	0.42	246	0.54		
69	0.41	134	1.50	247	2.31		
70	0.35	135	0.79	248	0.39		
77	1.15	136	1.12				
78	0.38	137	0.92				
79	1.15	146	0.41				
80	0.66	147	0.20				
81	0.64	148	0.80				
82	0.32	149	0.33				
83	0.23	150	0.29				
84	0.20	160	0.56				
91	1.10	161	0.26				
92	0.26	162	1.32				
93	0.59	163	0.36				
94	0.43	172	0.21				
95	0.34	174	0.28				
96	0.31	176	0.64				

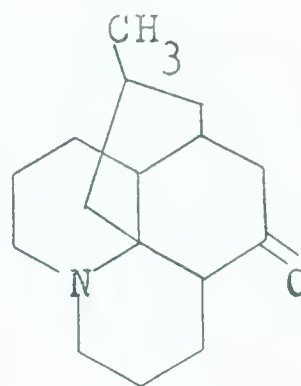
Lycopodine

C₁₆H₂₅ON

M.W. 247

Temperature: ~58°C

Electron Energy: 70 ev



m/e	%	25	m/e	%	25	m/e	%	25	m/e	%	25
27	1.20		97	0.18		174	0.21				
28	1.83		103	0.12		176	0.63				
29	1.25		104	0.12		177	0.16				
30	0.47		105	0.47		188	0.47				
32	0.13		106	0.54		189	0.16				
39	1.20		107	0.36		190	41.70				
40	0.29		108	0.52		191	5.27				
41	3.35		109	0.18		192	0.50				
42	1.42		110	0.15		204	0.82				
43	0.96		115	0.11		205	0.25				
44	0.46		117	0.26		218	0.16				
51	0.24		118	0.25		232	0.20				
52	0.21		119	0.26		244	0.12				
53	1.10		120	0.77		245	0.12				
54	0.87		121	0.35		246	0.52				
55	2.64		122	0.55		247	3.39				
56	0.56		123	0.35		248	0.53				
57	0.18		124	0.09							
65	0.55		130	0.13							
66	0.29		131	0.13							
67	1.03		132	0.35							
68	0.57		133	0.27							
69	0.44		134	1.32							
70	0.34		135	0.73							
77	1.02		136	1.05							
78	0.33		137	0.91							
79	1.06		138	0.12							
80	0.58		144	0.08							
81	0.66		146	0.33							
82	0.32		147	0.12							
83	0.22		148	0.74							
84	0.22		149	0.33							
91	1.00		150	0.28							
92	0.24		160	0.39							
93	0.56		161	0.20							
94	0.40		162	2.44							
95	0.35		163	0.35							
96	0.31		172	0.10							

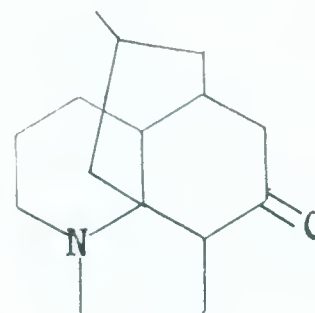
Epilycopodine

C₁₆H₂₅ON

M.W. 247

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.06	96	0.28	164	0.34		
27	0.80	97	0.12	174	0.19		
28	2.22	103	0.09	175	0.10		
29	1.07	104	0.10	176	2.03		
30	0.48	105	0.43	177	0.74		
32	0.25	106	0.62	178	0.10		
39	0.79	107	0.39	186	0.08		
40	0.21	108	0.88	188	0.28		
41	3.09	109	0.23	189	0.13		
42	1.50	110	0.14	190	20.60		
43	0.96	111	0.13	191	7.32		
44	0.41	115	0.06	192	0.33		
51	0.12	117	0.23	202	0.09		
52	0.13	118	0.24	204	3.18		
53	0.91	119	0.25	205	0.90		
54	0.91	120	0.26	206	0.09		
55	2.62	121	0.44	218	0.44		
56	0.54	122	0.70	219	0.74		
57	0.13	123	0.33	220	0.10		
65	0.42	124	0.06	232	0.86		
66	0.23	129	0.11	233	0.13		
67	1.10	130	0.13	245	0.05		
68	0.50	131	0.46	246	0.66		
69	0.35	132	0.45	247	2.71		
70	0.28	133	2.41	248	0.44		
77	0.87	134	3.72	249	0.04		
78	0.26	135	3.03				
79	1.05	136	4.66				
80	0.63	137	0.63				
81	0.50	146	0.26				
82	0.35	147	0.12				
83	0.19	148	0.72				
84	0.21	149	0.48				
91	0.92	150	0.23				
92	0.23	160	0.36				
93	0.55	161	0.22				
94	0.43	162	4.57				
95	0.39	163	2.18				

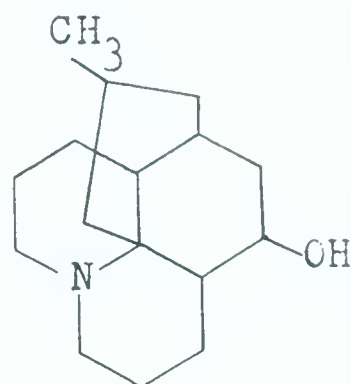
Dihydrolycopodine

C₁₆H₂₇ON

M.W. 249

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	1.17	105	0.47	188	0.74		
28	2.54	106	0.42	190	4.46		
29	1.50	107	0.31	191	10.60		
30	0.60	108	0.39	192	26.80		
39	1.25	117	0.36	193	3.21		
40	0.29	118	0.35	202	0.18		
41	3.40	119	0.26	204	0.25		
42	1.30	120	0.61	205	0.22		
43	1.09	121	0.26	206	0.61		
44	0.95	122	0.50	216	0.10		
51	0.26	123	0.28	230	0.31		
52	0.21	130	0.26	231	0.26		
53	1.06	131	0.24	232	0.33		
54	0.81	132	0.42	234	0.15		
55	2.02	133	0.25	246	0.53		
56	0.57	134	0.89	247	0.57		
57	0.42	135	0.43	248	0.40		
65	0.57	136	1.03	249	1.02		
66	0.28	137	1.28	250	0.17		
67	0.97	138	0.17				
68	0.49	144	0.24				
69	0.38	146	1.90				
70	0.38	147	0.38				
77	1.02	148	0.81				
78	0.32	149	0.29				
79	0.99	150	0.25				
80	0.53	160	0.59				
81	0.61	162	0.95				
82	0.31	163	0.35				
83	0.20	164	0.36				
84	0.21	172	0.45				
91	1.09	174	3.76				
92	0.25	175	0.72				
93	0.52	176	0.50				
94	0.38	178	0.17				
95	0.28	185	0.91				
96	0.29	186	0.28				

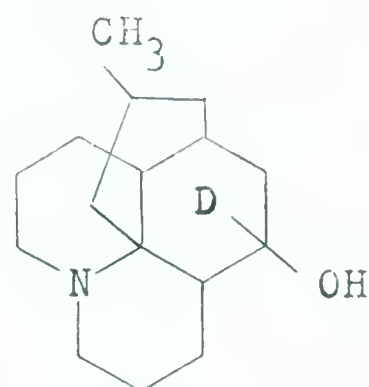
5-Deuterodihydrolycopodine

C₁₆H₂₆DON

M.w. 250

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.14	92	0.43	146	2.23	207	0.43
27	0.71	93	0.45	147	1.85	208	0.08
28	1.88	94	0.36	148	0.93	217	0.14
29	0.74	95	0.26	149	0.41	228	0.08
30	0.58	96	0.28	150	0.21	229	0.17
31	0.07	97	0.18	151	0.09	230	0.20
32	0.13	98	0.07	158	0.17	231	0.71
39	0.82	103	0.13	159	0.15	232	0.52
40	0.26	104	0.14	160	0.51	233	0.31
41	2.19	105	0.40	161	0.36	235	0.09
42	1.23	106	0.41	162	0.91	244	0.14
43	1.46	107	0.26	163	0.48	245	0.14
44	1.44	108	0.34	164	0.21	246	0.21
45	0.09	109	0.17	165	0.26	247	0.95
51	0.18	110	0.13	166	0.08	248	0.54
52	0.14	111	0.16	170	0.10	249	0.45
53	0.64	115	0.15	171	0.11	250	0.89
54	0.57	116	0.13	172	0.49	251	0.17
55	1.24	117	0.34	173	0.59		
56	0.54	118	0.41	174	4.53		
57	0.23	119	0.32	175	5.40		
58	0.39	120	0.52	176	1.19		
60	0.39	121	0.29	177	0.57		
65	0.42	122	0.46	178	0.11		
66	0.26	123	0.31	179	0.10		
67	0.68	124	0.13	186	0.14		
68	0.44	128	0.08	187	0.11		
69	0.29	129	0.11	188	0.64		
70	0.32	130	0.26	189	0.44		
71	0.10	131	0.33	190	4.95		
77	0.75	132	0.47	191	1.60		
78	0.36	133	0.34	192	3.51		
79	0.79	134	0.83	193	19.90		
80	0.57	135	0.41	194	3.00		
81	0.46	136	0.96	195	0.29		
82	0.33	137	1.15	202	0.15		
83	0.19	138	0.19	203	0.14		
84	0.28	143	0.10	204	0.19		
85	0.08	144	0.26	205	0.25		
91	0.88	145	0.25	206	0.15		

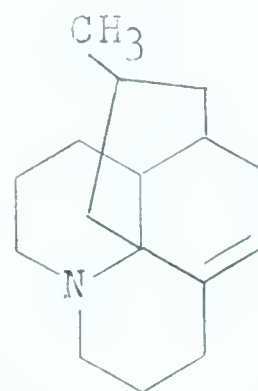
Anhydrodihydrolycopodine

$C_{16}H_{25}N$

M.W. 231

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
27	0.79	95	0.15	147	1.62	228	0.50
28	1.73	96	0.16	148	0.52	229	0.35
29	0.86	97	0.10	149	0.18	230	0.96
30	0.36	103	0.31	150	0.16	231	1.92
32	0.22	104	0.30	156	0.17	232	0.39
39	1.03	105	0.71	157	0.15		
40	0.22	106	0.39	158	0.48		
41	3.41	107	0.19	159	0.22		
42	0.94	108	0.19	160	1.11		
43	0.46	109	0.09	161	0.31		
44	0.63	110	0.09	162	0.26		
51	0.30	111	0.13	163	0.09		
52	0.21	115	0.45	164	0.11		
53	0.81	116	0.24	165	0.19		
54	0.49	117	0.85	170	0.42		
55	1.02	118	0.88	171	0.16		
56	0.51	119	0.40	172	2.54		
57	0.10	120	0.57	173	0.75		
63	0.11	121	0.22	174	23.20		
65	0.68	122	0.36	175	3.50		
66	0.24	123	0.15	176	1.27		
67	0.16	124	0.09	177	0.17		
68	0.07	128	0.23	184	0.13		
69	0.17	129	0.25	186	0.56		
70	0.18	130	0.72	187	0.16		
77	1.19	131	0.70	188	2.17		
78	0.41	132	0.72	189	0.47		
79	0.97	133	0.35	190	0.24		
80	0.42	134	0.53	200	0.25		
81	0.36	135	0.23	201	0.09		
82	0.19	136	0.54	202	2.45		
83	0.09	137	1.19	203	0.61		
84	0.16	138	0.13	204	1.15		
89	0.10	142	0.16	205	0.17		
91	1.91	143	0.25	214	0.17		
92	0.32	144	1.01	216	0.86		
93	0.43	145	0.39	217	0.17		
94	0.26	146	11.60	218	0.10		

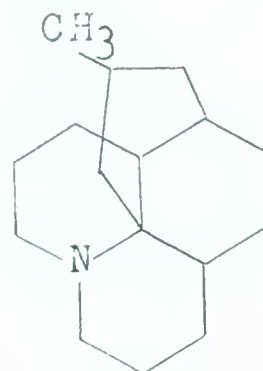
Lycopodane

$C_{16}H_{27}N$

M.W. 233

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.08	93	0.60	158	0.10		
27	0.66	94	0.39	160	0.37		
28	3.37	95	0.28	161	0.18		
29	0.89	96	0.27	162	0.72		
30	0.37	97	0.14	163	0.27		
32	0.24	103	0.12	164	0.12		
35	0.10	104	0.11	172	0.24		
36	0.09	105	0.46	173	0.14		
39	0.85	106	0.40	174	2.22		
40	0.22	107	0.32	175	0.65		
41	2.85	108	0.37	176	42.70		
42	0.24	109	0.17	177	6.04		
47	0.16	110	0.17	178	0.41		
51	0.16	111	0.08	186	0.09		
52	0.14	115	0.12	188	0.34		
53	0.81	117	0.62	189	0.19		
54	0.61	118	0.27	190	1.62		
55	1.48	119	0.58	191	0.27		
56	0.44	120	0.69	202	0.08		
57	0.10	121	0.42	204	0.34		
58	0.17	122	0.59	205	0.19		
65	0.44	123	0.32	216	0.09		
66	0.22	130	0.18	218	0.22		
67	1.01	131	0.21	230	0.81		
68	0.43	132	0.37	231	0.50		
69	0.29	133	0.27	232	0.61		
70	0.27	134	0.83	233	1.55		
77	0.87	135	0.40	234	0.27		
78	0.25	136	1.08				
79	1.02	137	1.27				
80	0.50	138	0.14				
81	0.60	144	0.14				
82	0.36	145	0.10				
83	0.38	146	0.84				
84	0.36	147	0.27				
85	0.19	148	1.65				
91	1.05	149	0.47				
92	0.24	150	0.29				

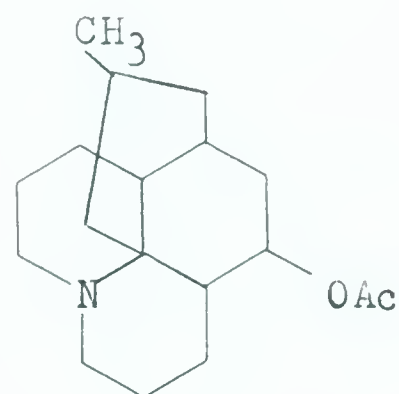
Dihydrolycopodine Acetate

$C_{16}H_{27}O_2N$

M.w. 291

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	1.00	103	0.24	161	0.28		
28	1.66	104	0.25	162	0.96		
29	1.20	105	0.66	163	0.34		
30	0.37	106	0.39	170	0.44		
32	0.30	107	0.17	171	0.13		
39	1.26	108	0.15	172	2.59		
40	0.33	115	0.35	173	0.75		
41	2.84	116	0.18	174	23.90		
42	1.71	117	0.69	175	7.98		
43	2.71	118	0.67	176	1.24		
44	4.59	119	0.31	186	0.43		
45	1.74	120	0.49	187	0.13		
51	0.36	121	0.19	188	1.54		
52	0.26	122	0.25	189	0.34		
53	0.91	123	0.13	190	0.35		
54	0.53	128	0.20	202	0.24		
55	1.02	129	0.23	203	0.12		
56	0.36	130	0.64	216	0.61		
60	0.91	131	0.57	217	0.09		
63	0.13	132	0.72	228	0.64		
65	0.70	133	0.37	229	0.46		
66	0.26	134	0.87	230	1.03		
67	0.70	135	0.31	231	2.00		
68	0.30	136	0.31	232	0.52		
69	0.13	137	0.57	234	0.89		
70	0.15	142	0.20	235	0.13		
77	1.20	143	0.25	244	0.03		
78	0.43	144	0.81	246	0.055		
79	0.95	145	0.37	248	0.041		
80	0.42	146	7.49	288	0.12		
81	0.35	147	1.08	289	0.13		
82	0.16	148	0.77	290	0.050		
91	1.56	149	0.34	291	0.155		
92	0.28	156	0.15	292	0.031		
93	0.39	157	0.12				
94	0.22	158	0.38				
95	0.11	159	0.17				
96	0.09	160	0.92				

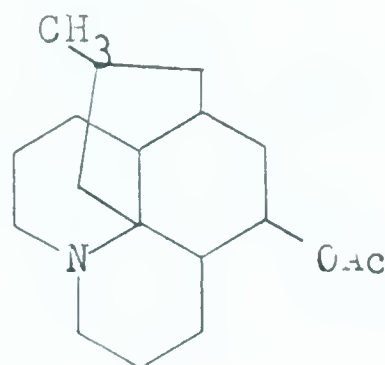
Dihydrolycopodine Acetate

C₁₈H₂₉O₂N

M.W. 291

Temperature: ~70°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	0.87	104	0.22	189	0.32		
28	1.05	105	0.61	190	1.11		
29	1.25	106	0.38	192	0.24		
30	0.42	108	0.24	202	0.22		
39	1.05	115	0.26	216	0.30		
40	0.24	117	0.61	230	1.37		
41	2.81	118	0.61	231	2.34		
42	1.39	119	0.32	232	1.43		
43	4.20	120	0.54	233	0.26		
44	0.65	122	0.30	234	7.23		
45	1.78	130	0.46	235	1.13		
51	0.24	131	0.40	246	0.30		
53	0.81	132	0.54	288	0.05		
54	0.52	133	0.24	289	0.091		
55	1.33	134	0.69	290	0.131		
56	0.44	135	0.28	291	0.77		
60	1.03	136	0.52	292	0.131		
65	0.57	137	0.85				
66	0.20	144	0.50				
67	0.69	145	0.22				
68	0.32	146	6.34				
69	0.24	147	0.97				
70	0.24	148	0.69				
77	1.03	149	0.34				
78	0.32	158	0.26				
79	0.91	160	0.87				
80	0.42	161	0.30				
81	0.46	162	0.46				
82	0.22	163	0.20				
84	0.20	172	1.25				
91	1.47	173	0.61				
92	0.26	174	24.8				
93	0.46	175	4.44				
94	0.26	176	1.51				
95	0.20	186	0.24				
96	0.20	188	1.47				

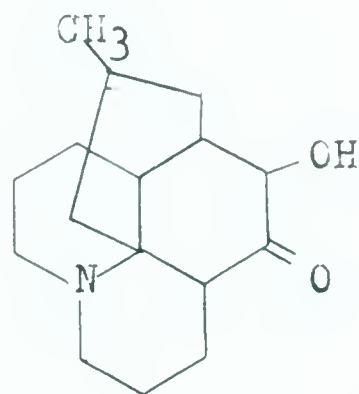
6 β -Hydroxylycopodine

C₁₆H₂₅O₂N

M.W. 263

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	0.94	95	0.29	158	0.20	233	0.24
28	4.36	96	0.31	159	0.11	234	0.34
29	1.31	97	0.23	160	1.25	235	0.19
30	0.53	103	0.16	161	0.38	245	0.13
31	0.20	104	0.15	162	1.07	246	0.24
32	0.31	105	0.45	163	0.64	248	0.15
39	1.00	106	0.44	164	0.48	249	0.15
40	0.28	107	0.34	165	0.12	258	0.11
41	2.54	108	0.46	172	0.22	259	0.21
42	1.14	109	0.20	173	0.12	260	0.15
43	0.82	110	0.17	174	0.97	261	0.51
44	0.78	115	0.16	175	0.28	262	0.35
51	0.23	116	0.09	176	2.32	263	1.50
52	0.19	117	0.33	177	1.39	264	0.12
53	0.92	118	0.29	178	2.83		
54	0.66	119	0.24	179	0.50		
55	2.12	120	0.67	180	0.09		
56	0.53	121	0.33	186	0.33		
57	0.42	122	0.63	188	2.38		
58	0.09	123	0.34	189	0.44		
65	0.54	124	0.11	190	1.40		
66	0.27	130	0.23	191	0.29		
67	0.86	131	0.22	192	3.91		
68	0.45	132	0.49	193	0.55		
69	0.38	133	0.35	200	0.11		
70	0.37	134	0.92	201	0.16		
77	0.96	135	0.49	202	1.76		
78	0.31	136	0.96	203	0.36		
79	0.93	137	0.76	204	6.34		
80	0.54	138	0.12	205	1.30		
81	0.59	144	0.15	206	16.30		
82	0.34	145	0.12	207	2.12		
83	0.22	146	0.70	208	0.24		
84	0.20	147	0.22	216	0.32		
91	0.94	148	0.94	218	1.18		
92	0.22	149	0.36	219	0.18		
93	0.51	150	0.59	220	0.41		
94	0.41	151	0.16	231	0.11		

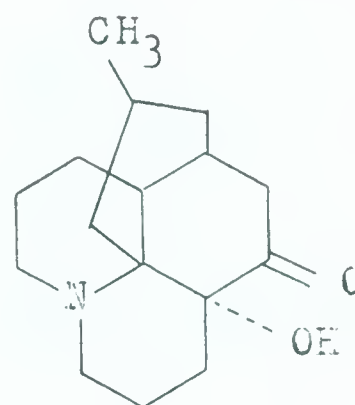
Flabelliformine

$C_{16}H_{25}O_2N$

M.W. 263

Temperature: 200°C

Electron energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
27	1.41	98	0.19	160	1.71	248	0.44
28	1.42	103	0.19	162	1.03	261	0.17
29	1.21	104	0.17	163	0.36	262	0.50
30	0.62	105	0.46	164	5.36	263	2.62
39	1.62	106	0.45	165	0.90	264	0.50
40	0.37	107	0.30	172	0.31		
41	4.36	108	0.36	174	0.75		
42	1.79	109	0.30	175	0.22		
43	1.71	110	0.24	176	1.08		
44	1.53	113	0.19	177	0.56		
51	0.42	115	0.19	178	1.11		
52	0.34	117	0.45	179	0.24		
53	1.43	118	0.36	184	0.22		
54	0.90	119	0.24	186	1.62		
55	2.08	120	0.64	187	0.34		
56	0.61	121	0.25	188	10.80		
57	0.22	122	0.87	189	1.59		
65	0.67	123	0.31	190	3.19		
66	0.31	124	0.14	191	0.40		
67	0.93	130	0.40	200	0.19		
68	0.56	131	0.36	202	0.43		
69	0.54	132	0.37	204	0.31		
70	0.31	133	0.44	205	0.20		
71	0.24	134	1.02	206	1.64		
77	1.10	135	0.49	207	0.22		
78	0.40	136	1.15	216	0.25		
79	0.97	137	1.51	217	0.14		
80	0.59	138	0.26	218	0.17		
81	0.61	144	0.24	220	0.27		
82	0.34	146	0.60	221	0.42		
83	0.21	147	0.27	233	0.70		
91	1.03	148	0.80	234	0.19		
92	0.25	149	0.59	242	0.55		
93	0.54	150	1.10	243	0.36		
94	0.44	151	0.52	244	0.37		
95	0.37	152	0.46	245	0.76		
96	0.31	153	0.21	246	0.90		
97	0.30	158	0.41	247	0.26		

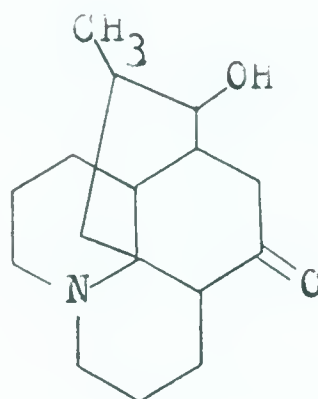
Clavolonine

C₁₆H₂₅O₂N

M.W. 263

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
26	0.07	93	0.49	172	0.20		
27	1.54	94	0.45	174	0.47		
28	1.73	95	0.32	176	0.29		
29	1.68	96	0.32	178	0.16		
30	0.63	97	0.17	186	0.35		
31	0.29	103	0.14	188	1.92		
39	1.40	104	0.13	189	0.50		
40	0.32	105	0.45	190	40.90		
41	3.30	106	0.51	191	5.20		
42	1.54	107	0.36	192	1.27		
43	1.40	108	0.52	193	0.14		
44	0.86	109	0.20	200	0.06		
45	0.12	110	0.15	202	0.17		
51	0.29	117	0.29	204	0.10		
52	0.25	118	0.27	206	0.07		
53	1.22	119	0.24	218	0.11		
54	1.05	120	0.68	220	0.47		
55	1.38	121	0.32	221	0.10		
56	0.62	122	0.55	230	0.08		
57	0.60	123	0.23	232	0.04		
58	0.13	130	0.20	234	0.04		
65	0.62	131	0.21	244	0.09		
66	0.32	132	0.48	245	0.09		
67	1.01	133	0.39	246	0.16		
68	0.57	134	1.50	247	0.04		
69	0.38	135	0.74	248	0.07		
70	0.44	136	1.43	260	0.08		
71	0.15	137	2.04	261	0.34		
77	1.06	138	0.47	262	0.38		
78	0.34	146	0.50	263	0.65		
79	1.01	147	0.23	264	0.10		
80	0.62	148	0.55				
81	0.62	149	0.29				
82	0.37	150	0.35				
83	0.27	160	0.98				
84	0.18	161	0.32				
91	0.94	162	2.50				
92	0.24	163	0.59				

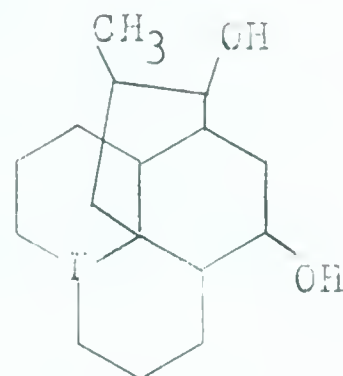
Dihydroclavolonine (Deacetyl Fawcettine)

$C_{16}H_{27}O_2N$

M.w. 265

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.08	93	0.43	146	3.01	214	0.07
27	0.70	94	0.36	147	0.64	216	0.05
28	0.49	95	0.28	148	0.68	218	0.09
29	0.89	96	0.33	149	0.35	220	0.18
30	0.51	97	0.17	150	0.33	222	0.25
31	0.15	98	0.08	151	0.09	228	0.08
39	0.77	103	0.14	158	0.17	229	0.08
40	0.16	104	0.11	159	0.10	230	0.19
41	2.12	105	0.42	160	0.72	232	0.23
42	0.87	106	0.32	161	0.21	244	0.15
43	1.01	107	0.51	162	1.10	245	0.14
44	1.02	108	0.44	163	0.39	246	0.45
45	0.15	109	0.20	164	0.37	247	0.53
51	0.18	110	0.18	165	0.11	248	0.25
52	0.13	111	0.15	166	0.11	261	0.10
53	0.65	115	0.16	170	0.13	262	0.16
54	0.53	116	0.09	172	0.73	263	0.48
55	1.34	117	0.34	173	0.31	264	0.19
56	0.44	118	0.33	174	5.76	265	0.23
57	0.37	119	0.26	175	1.75	266	0.03
58	0.12	120	0.56	176	1.20		
63	0.05	121	0.33	177	0.24		
65	0.44	122	0.75	178	1.34		
66	0.18	123	0.32	179	0.28		
67	0.69	124	0.12	186	0.19		
68	0.37	128	0.09	187	0.08		
69	0.30	129	0.10	188	0.72		
70	0.36	130	0.24	189	0.19		
71	0.10	131	0.29	190	12.30		
77	0.81	132	0.40	191	1.86		
78	0.23	133	0.44	192	22.50		
79	0.79	134	0.90	193	1.63		
80	0.43	135	0.40	194	0.16		
81	0.45	136	1.64	200	0.09		
82	0.29	137	2.77	202	0.17		
83	0.19	138	0.33	203	0.18		
84	0.23	143	0.09	204	0.29		
91	0.96	144	0.27	205	0.09		
92	0.19	145	0.15	206	0.20		

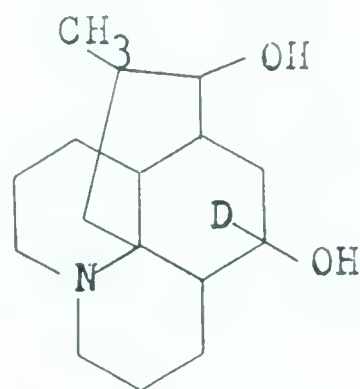
5-Deuterodihydroclavolone

$C_{16}H_{26}DO_2N$

M.w. 266

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.10	92	0.45	148	0.71	231	0.12
27	1.08	93	0.42	149	0.49	233	0.13
28	1.30	94	0.42	150	0.30	245	0.11
29	1.32	95	0.27	151	0.12	246	0.15
30	0.78	96	0.29	158	0.17	247	0.34
31	0.29	97	0.17	159	0.14	248	0.36
32	0.12	103	0.13	160	0.60	249	0.20
39	1.06	104	0.14	161	0.31	261	0.11
40	0.33	105	0.86	162	0.94	262	0.14
41	1.32	106	0.42	163	0.38	263	0.24
42	1.54	107	0.29	164	0.20	264	0.28
43	1.38	108	0.45	165	0.19	265	0.19
44	1.79	109	0.21	172	0.32	266	0.18
45	0.21	110	0.16	173	0.41	267	0.04
51	0.22	111	0.14	174	1.84		
52	0.20	115	0.13	175	2.19		
53	0.87	116	0.12	176	1.13		
54	0.85	117	0.27	177	0.81		
55	1.69	118	0.35	178	0.24		
56	0.68	119	0.29	186	0.12		
57	0.46	120	0.59	187	0.10		
58	0.29	121	0.36	188	0.70		
65	0.43	122	0.59	189	0.30		
66	0.29	123	0.30	190	12.30		
67	0.71	124	0.14	191	2.97		
68	0.54	130	0.21	192	1.20		
69	0.30	131	0.25	193	17.70		
70	0.37	132	0.43	194	3.20		
71	0.13	133	0.34	195	0.46		
77	0.77	134	0.93	202	0.11		
78	0.39	135	0.61	203	0.17		
79	0.75	136	1.40	204	0.11		
80	0.62	137	2.61	205	0.17		
81	0.49	138	0.35	206	0.09		
82	0.36	144	0.19	207	0.17		
83	0.20	145	0.19	220	0.17		
84	0.20	146	1.04	221	0.11		
91	0.76	147	1.36	223	0.23		

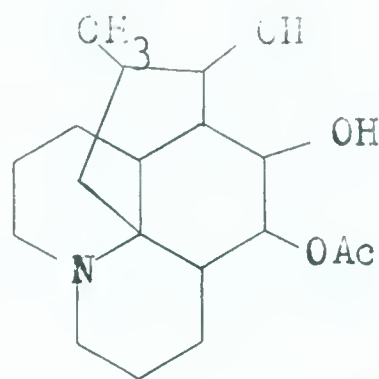
Fawcettine

$C_{18}H_{29}O_3N$

M.W. 307

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.16	92	0.26	145	0.26	229	0.19
27	1.07	93	0.34	146	8.10	230	0.27
28	1.08	94	0.23	147	1.17	232	0.19
29	1.38	95	0.16	148	0.62	234	0.29
30	0.41	96	0.15	149	0.43	245	0.10
31	0.35	103	0.23	150	0.31	246	0.20
39	1.18	104	0.23	156	0.12	247	0.35
40	0.29	105	0.45	157	0.10	248	0.62
41	2.54	106	0.32	158	0.30	249	0.13
42	1.57	107	0.19	159	0.13		
43	4.76	108	0.20	160	0.73		
44	1.18	109	0.13	161	0.17		
45	2.74	110	0.08	162	0.33		
51	0.32	111	0.10	164	0.17		
52	0.22	115	0.32	170	0.31		
53	0.79	116	0.17	171	0.15		
54	0.49	117	0.57	172	1.76		
55	0.86	118	0.61	173	0.72		
56	0.34	119	0.25	174	21.60		
57	0.34	120	0.42	175	3.80		
58	0.27	121	0.25	176	3.80		
60	1.41	122	0.38	177	0.73		
63	0.13	123	0.30	178	0.30		
65	0.62	124	0.17	179	0.19		
66	0.24	128	0.17	186	0.33		
67	0.60	129	0.19	187	0.12		
68	0.32	130	0.58	188	0.33		
69	0.20	131	0.46	189	0.09		
70	0.21	132	0.52	190	0.26		
77	1.03	133	0.23	192	0.21		
78	0.35	134	0.54	200	0.09		
79	0.75	135	0.33	202	0.11		
80	0.37	136	0.73	204	0.51		
81	0.32	137	2.12	205	0.10		
82	0.17	138	0.22	206	0.11		
83	0.12	142	0.13	213	0.15		
84	0.11	143	0.18	218	0.68		
91	1.55	144	0.64	228	0.13		

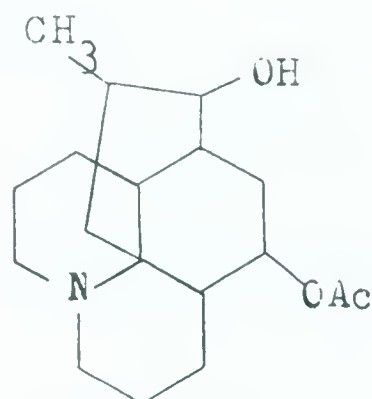
α-Lofoline

C₁₈H₂₉O₃N

M.W. 307

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	1.01	96	0.15	172	2.21		
28	1.21	103	0.22	173	0.79		
29	1.31	104	0.24	174	24.60		
30	0.43	105	0.49	175	4.03		
31	0.32	106	0.33	176	2.15		
39	1.17	107	0.18	186	0.31		
40	0.26	108	0.21	188	0.43		
41	2.50	115	0.35	190	0.29		
42	1.42	117	0.68	192	0.18		
43	3.89	118	0.69	202	0.15		
44	1.65	119	0.32	204	0.52		
45	2.21	120	0.51	205	0.12		
51	0.29	121	0.28	206	0.23		
52	0.19	122	0.46	214	0.22		
53	0.78	123	0.28	218	0.08		
54	0.47	128	0.17	228	0.17		
55	0.97	129	0.21	229	0.24		
56	0.35	130	0.62	230	0.58		
57	0.38	131	0.50	232	0.22		
60	1.14	132	0.61	234	1.46		
65	0.60	133	0.28	235	0.28		
66	0.22	134	0.58	246	0.18		
67	0.60	135	0.33	247	0.42		
68	0.32	136	0.71	248	0.69		
69	0.16	137	1.22	249	0.24		
70	0.25	143	0.19				
77	1.04	144	0.69				
78	0.36	145	0.26				
79	0.79	146	8.00				
80	0.38	147	1.17				
81	0.36	148	0.61				
82	0.19	149	0.39				
83	0.24	158	0.32				
91	1.57	160	0.92				
92	0.26	161	0.28				
93	0.35	162	0.38				
94	0.24	170	0.33				
95	0.17	171	0.17				

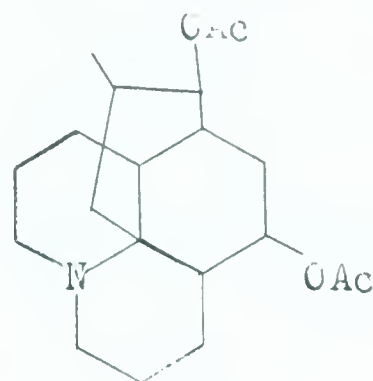
C-Acetyllofoline

$C_{20}H_{31}O_4N$

M.W. 349

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
26	0.07	89	0.12	143	0.17	212	0.07
27	0.34	91	2.54	144	0.43	214	0.64
28	2.7	92	0.48	145	0.23	215	0.32
29	0.59	93	0.90	146	5.88	216	0.10
30	0.33	94	0.59	147	0.67	218	0.09
31	0.17	95	0.57	148	0.69	220	0.09
32	0.90	96	0.51	149	0.30	228	0.33
39	0.98	97	0.37	150	0.15	229	0.36
40	0.35	103	0.17	156	0.09	230	1.51
41	3.52	104	0.15	157	0.11	231	0.33
42	2.06	105	0.50	158	0.29	232	0.32
43	10.5	106	0.28	159	0.18	233	0.12
44	1.47	107	0.20	160	0.88	234	7.92
45	2.52	108	0.27	161	0.25	235	1.10
51	0.25	109	0.17	162	0.34	236	0.16
52	0.18	110	0.13	163	0.09	246	0.44
53	1.02	111	0.10	164	0.12	247	0.14
54	0.82	115	0.22	170	0.22	248	0.36
55	2.34	116	0.12	171	0.11	264	0.29
56	0.91	117	0.46	172	1.11	274	0.36
57	0.93	118	0.47	173	0.68	275	0.07
58	0.17	119	0.31	174	17.3	288	0.26
60	1.46	120	0.48	175	1.88	289	0.74
65	0.74	121	0.22	176	0.97	290	11.5
66	0.30	122	0.38	177	0.11	291	0.20
67	1.31	123	0.15	184	0.10	306	0.07
68	0.62	124	0.07	185	0.07	347	0.07
69	0.65	128	0.13	186	0.52	349	0.31
70	0.65	129	0.18	187	0.17		
71	0.38	130	0.36	188	0.48		
77	1.47	131	0.43	189	0.14		
78	0.46	132	0.50	190	1.16		
79	1.61	133	0.26	191	0.17		
80	0.76	134	0.60	192	0.08		
81	1.06	135	0.26	200	0.20		
82	0.57	136	0.78	201	0.08		
83	0.50	137	1.38	202	0.32		
84	0.81	138	0.13	204	0.64		
85	0.28	142	0.09	205	0.11		

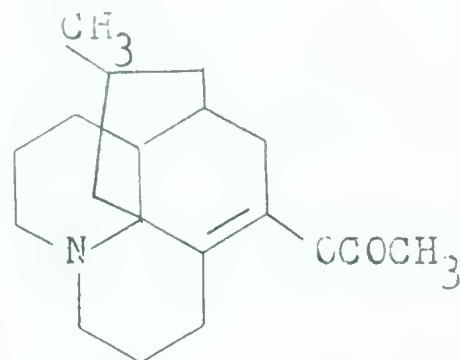
Lyconodine Enol Acetate

$C_{18}H_{27}O_2N$

M.W. 289

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
27	0.65	103	0.18	161	0.61		
28	1.09	104	0.19	162	3.66		
29	0.63	105	0.55	163	0.54		
30	0.38	106	0.51	170	0.13		
32	0.21	107	0.45	171	0.08		
39	0.81	108	0.30	172	1.18		
40	0.18	109	0.14	173	0.33		
41	2.22	115	0.19	174	0.29		
42	1.29	116	0.13	175	0.09		
43	1.99	117	0.42	176	0.28		
44	0.65	118	0.34	177	0.10		
51	0.47	119	0.29	186	0.76		
52	0.22	120	0.66	187	0.24		
53	0.82	121	0.24	188	1.83		
54	0.50	122	0.29	189	0.89		
55	1.19	123	0.11	190	27.90		
56	0.39	130	0.24	191	4.04		
57	0.15	131	0.24	192	0.34		
65	0.51	132	0.63	202	0.21		
66	0.23	133	0.51	203	0.11		
67	0.65	134	1.18	204	2.32		
68	0.30	135	0.38	205	0.44		
69	0.24	136	0.43	218	0.24		
70	0.23	137	0.37	230	0.45		
77	0.97	138	0.10	231	0.15		
78	0.34	144	0.27	232	12.10		
79	0.95	145	0.15	233	1.98		
80	0.48	146	0.67	234	0.21		
81	0.44	147	0.29	244	0.16		
82	0.18	148	0.55	246	1.26		
84	0.12	149	0.17	247	0.28		
91	1.02	150	0.24	289	1.30		
92	0.24	156	0.34	290	0.25		
93	0.43	157	0.21				
94	0.25	158	0.25				
95	0.19	159	0.18				
96	0.15	160	1.20				

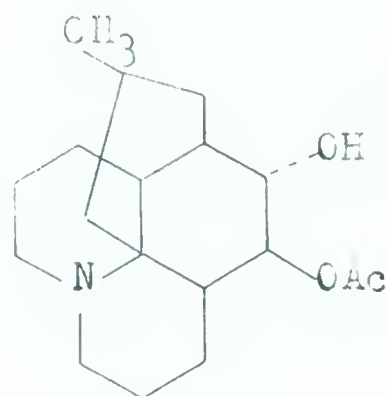
Lycoclavine

$C_{18}H_{29}O_3N$

M.W. 307

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.11	95	0.29	149	0.36	218	0.54
27	1.12	96	0.23	150	0.45	219	0.12
28	1.31	97	0.22	151	0.21	228	0.24
29	1.63	103	0.19	156	0.12	229	0.31
30	0.44	104	0.17	157	0.10	230	0.63
31	0.23	105	0.44	158	0.33	231	0.12
39	1.37	106	0.43	159	0.17	232	0.25
41	3.31	107	0.33	160	0.75	244	0.31
42	1.58	108	0.29	161	0.69	245	0.41
43	3.60	109	0.17	162	3.48	246	3.29
44	1.87	110	0.16	163	0.53	247	2.32
45	2.30	111	0.26	164	0.78	248	0.40
51	0.34	115	0.30	170	0.35	250	0.08
52	0.23	116	0.14	171	0.11	293	0.07
53	0.97	117	0.52	172	3.66		
54	0.62	118	0.47	173	0.70		
55	1.52	119	0.28	174	1.65		
56	0.46	120	0.60	175	0.31		
57	0.43	121	0.29	176	0.66		
60	1.16	122	0.48	177	0.16		
63	0.12	123	0.22	178	0.15		
65	0.64	124	0.10	184	0.10		
66	0.28	128	0.12	185	0.10		
67	0.89	129	0.14	186	0.59		
68	0.46	130	0.44	187	0.16		
69	0.38	131	0.30	188	1.37		
70	0.28	132	0.53	189	0.30		
71	0.11	133	0.35	190	11.10		
77	1.08	134	0.82	191	1.44		
78	0.38	135	0.36	192	0.99		
79	0.90	136	0.59	193	0.11		
80	0.51	137	0.51	200	0.10		
81	0.56	138	0.10	202	0.36		
82	0.29	142	0.10	203	0.38		
83	0.24	143	0.16	204	0.75		
84	0.14	144	0.74	205	0.28		
91	1.13	145	0.23	206	0.19		
92	0.26	146	1.20	208	0.37		
93	0.57	147	0.40	214	0.08		
94	0.38	148	0.87	216	0.14		

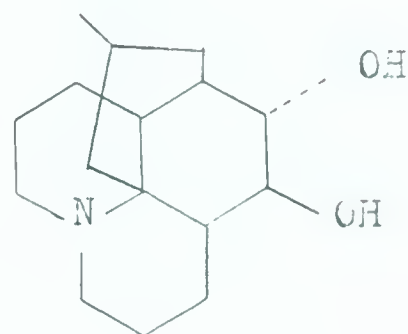
Deacetyllycoclavine

C₁₆H₂₇O₂N

M.W. 265

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
26	0.09	94	0.41	145	0.19	201	0.24
27	0.79	95	0.34	146	0.77	202	2.36
28	0.90	96	0.36	147	0.28	203	0.67
29	1.13	97	0.27	148	2.77	204	1.45
30	0.58	98	0.11	149	0.67	205	2.84
31	0.18	103	0.18	150	0.47	206	2.12
39	0.92	104	0.14	151	0.14	207	0.36
40	0.20	105	0.45	152	0.12	208	13.8
41	2.56	106	0.42	156	0.13	209	1.99
42	1.02	107	0.38	157	0.11	210	0.21
43	0.91	108	0.44	158	0.37	216	0.38
44	0.89	109	0.24	159	0.19	217	0.09
45	0.12	110	0.23	160	1.02	218	0.41
51	0.24	111	0.31	161	0.43	219	0.11
52	0.16	115	0.22	162	3.77	220	0.22
53	0.75	116	0.12	163	1.12	221	0.12
54	0.56	117	0.43	164	0.54	222	0.51
55	1.55	118	0.37	165	0.20	228	0.17
56	0.51	119	0.26	166	0.12	229	0.14
57	0.51	120	0.62	170	0.39	230	0.18
58	0.12	121	0.33	171	0.11	232	0.11
65	0.52	122	0.71	172	1.22	234	0.16
66	0.22	123	0.38	173	0.35	242	0.11
67	0.84	124	0.14	174	1.03	243	0.11
68	0.46	128	0.13	175	0.29	244	0.35
69	0.41	129	0.14	176	0.68	245	0.39
70	0.39	130	0.35	177	0.25	246	0.89
77	0.91	131	0.29	178	0.35	247	0.92
78	0.30	132	0.56	179	0.91	248	0.49
79	0.89	133	0.53	180	0.15	249	0.13
80	0.52	134	1.14	186	0.71	262	0.38
81	0.58	135	0.51	187	0.18	263	0.29
82	0.38	136	1.26	188	1.82	264	0.24
83	0.27	137	1.62	189	0.40	265	0.93
84	0.25	138	0.25	190	4.38	266	0.18
91	0.96	142	0.11	191	0.72		
92	0.23	143	0.15	192	0.49		
93	0.57	144	0.43	200	0.28		

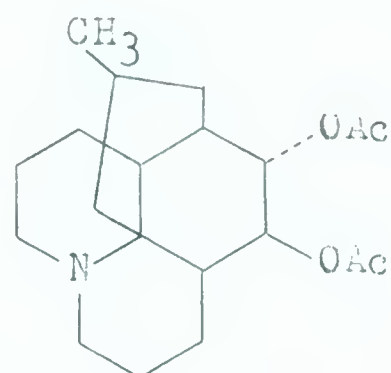
Lycoclavine Acetate

$C_{20}H_{31}O_4N$

M.w. 349

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
27	0.47	95	0.26	164	0.47	334	0.007
28	2.65	96	0.26	170	0.29	346	0.065
29	0.75	97	0.22	172	1.67	347	0.17
30	0.47	105	0.36	173	1.34	348	0.062
32	0.24	106	0.30	174	1.85	349	0.111
39	0.51	107	0.26	175	0.35	350	0.025
40	0.16	108	0.31	176	0.29		
41	1.96	109	0.17	178	0.15		
42	1.15	110	0.16	186	0.25		
43	5.89	111	0.11	188	0.66		
44	1.07	115	0.15	189	0.19		
45	0.42	117	0.26	190	14.70		
51	0.11	118	0.22	191	2.38		
52	0.09	119	0.17	192	0.20		
53	0.51	120	0.42	202	0.30		
54	0.44	121	0.20	204	0.36		
55	1.39	122	0.34	205	0.38		
56	0.45	123	0.21	218	0.11		
57	0.29	130	0.21	228	0.81		
60	0.20	131	0.20	229	0.50		
65	0.29	132	0.32	230	16.50		
66	0.12	133	0.26	231	3.12		
67	0.70	134	0.67	232	2.13		
68	0.36	135	0.32	244	0.18		
69	0.31	136	0.62	246	0.41		
70	0.31	137	0.50	247	0.43		
77	0.55	144	0.39	248	0.51		
78	0.17	145	0.16	261	0.019		
79	0.62	146	1.00	263	0.025		
80	0.34	147	0.25	275	0.013		
81	0.47	148	0.91	285	0.11		
82	0.26	149	0.25	287	0.35		
83	0.20	150	0.31	288	0.48		
84	0.25	158	0.19	289	0.84		
91	0.74	160	0.47	291	4.31		
92	0.15	161	0.21	292	0.53		
93	0.42	162	1.49	304	0.014		
94	0.29	163	0.39	306	0.063		

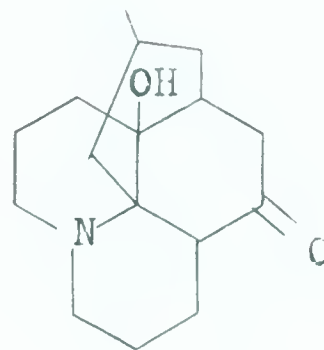
Lycodoline

$C_{16}H_{25}O_2N$

M.W. 263

Temperature: 200°C

Electron Energy: 70 ev



m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
27	1.59	94	0.42	147	0.35	205	0.10
28	1.36	95	0.49	148	0.67	206	1.56
29	1.36	96	1.31	149	0.41	207	0.72
30	0.71	97	0.58	150	1.74	208	0.12
31	0.12	98	0.21	151	2.96	216	0.22
39	1.51	99	0.25	152	3.24	217	0.58
40	0.34	103	0.09	153	1.04	218	0.60
41	4.52	104	0.08	154	0.12	219	0.09
42	1.80	105	0.34	158	0.23	220	2.12
43	2.38	106	0.27	159	0.15	221	0.63
44	1.56	107	0.29	160	0.73	222	0.08
45	0.09	108	0.36	161	0.32	230	0.23
51	0.24	109	0.35	162	1.26	233	0.15
52	0.21	110	0.36	163	0.31	234	0.24
53	1.23	111	0.19	164	0.80	235	1.03
54	0.76	112	0.10	165	0.95	236	0.15
55	2.50	117	0.21	166	0.39	242	0.14
56	0.86	118	0.17	172	0.20	243	0.06
57	0.35	119	0.15	173	0.10	244	0.74
58	0.12	120	0.37	174	0.52	245	0.42
65	0.53	121	0.20	175	0.21	246	4.06
66	0.29	122	0.63	176	0.63	247	0.69
67	1.08	123	1.92	177	0.27	248	0.82
68	0.95	124	1.56	178	1.93	249	0.14
69	1.07	125	0.20	179	0.68	261	0.53
70	0.75	130	0.21	180	0.39	262	0.61
71	0.21	131	0.20	186	0.28	263	4.55
77	0.68	132	0.37	187	0.08	264	0.79
78	0.24	133	0.24	188	0.66	265	0.07
79	0.73	134	0.58	189	0.28		
80	0.50	135	0.25	190	3.43		
81	0.63	136	0.75	191	0.50		
82	0.51	137	0.50	192	2.22		
83	0.48	138	0.28	193	0.22		
84	0.34	139	0.10	200	0.22		
91	0.69	144	0.16	202	0.51		
92	0.19	145	0.13	203	0.27		
93	0.46	146	0.49	204	0.60		

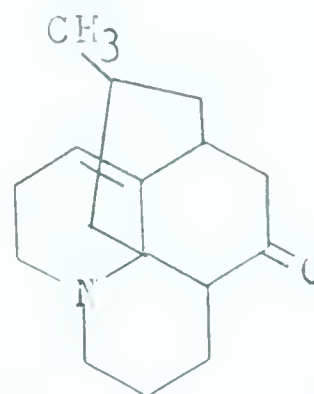
Dehydrolycodoline

C₁₆H₂₃ON

M.W. 245

Temperature: 200°C

Electron Energy: 70 ev



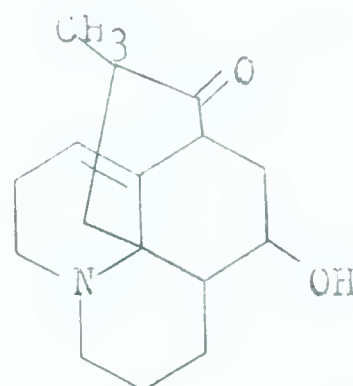
m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.14	78	0.45	123	0.91	177	0.11
27	1.08	79	0.91	124	0.12	184	0.11
28	1.06	80	0.42	127	0.10	186	0.44
29	1.07	81	0.32	128	0.22	187	0.21
30	0.31	82	0.19	129	0.23	188	3.85
31	0.23	83	0.29	130	0.68	189	1.62
32	0.13	84	0.11	131	0.55	190	0.96
39	1.08	85	0.21	132	1.12	191	0.17
40	0.22	87	0.07	133	0.60	200	0.48
41	2.21	89	0.15	134	0.67	201	0.28
42	1.46	90	0.09	135	0.36	202	6.66
43	2.72	91	1.37	136	0.21	203	4.89
44	0.87	92	0.29	141	0.10	204	0.71
45	0.40	93	0.38	142	0.13	214	0.11
51	0.36	94	0.23	143	0.23	216	1.12
52	0.27	95	0.19	144	0.51	217	0.69
53	0.75	96	0.13	145	0.34	218	0.12
54	0.42	97	0.18	146	1.18	228	0.14
55	1.74	98	0.07	147	0.74	230	1.59
56	0.50	99	0.08	148	0.55	231	0.25
57	0.69	101	0.26	149	0.40	242	0.22
58	0.38	102	0.11	150	1.28	243	0.33
59	0.22	103	0.38	151	0.16	244	5.89
61	0.12	104	0.34	156	0.18	245	6.66
63	0.14	105	0.65	157	0.13	246	0.64
64	0.08	106	0.40	158	0.78	247	0.11
65	0.67	107	0.20	159	0.49		
66	0.24	108	0.14	160	4.56		
67	0.50	109	0.10	161	2.50		
68	0.26	111	0.11	162	0.76		
69	0.33	115	0.47	163	0.19		
70	0.31	116	0.23	170	0.18		
71	0.41	117	0.89	171	0.09		
72	0.13	118	0.65	172	0.48		
73	0.24	119	0.44	173	0.26		
75	0.09	120	0.53	174	2.54		
76	0.06	121	0.24	175	0.55		
77	1.21	122	0.40	176	0.77		

Acrifoline $C_{16}H_{23}O_2N$

M.W. 261

Temperature: 200°C

Electron Energy: 70 ev



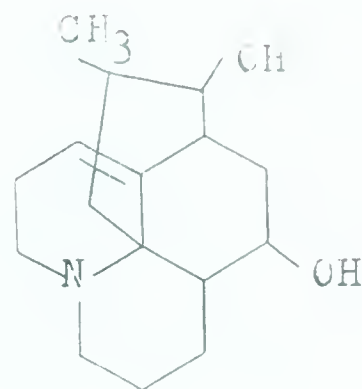
m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	0.84	86.5	0.13	146	2.40	217	0.29
28	2.34	89	0.09	147	1.39	218	1.05
29	0.81	90	0.08	148	0.36	219	0.16
30	0.38	91	1.36	149	0.16	230	0.12
31	0.15	92	0.27	150	0.12	231	0.33
32	0.29	93	0.30	154	0.10	232	1.18
39	1.02	94	0.21	156	0.21	233	3.98
40	0.24	95	0.08	157	0.20	234	0.58
41	2.02	96	0.08	158	0.64	242	0.26
42	1.44	103	0.30	159	0.42	244	0.17
43	0.76	104	0.29	160	1.84	246	0.32
44	1.44	105	0.50	161	0.76	260	0.17
45	0.13	106	0.52	162	1.09	261	1.93
51	0.34	107	0.21	163	0.60	262	0.31
52	0.25	108	0.12	164	0.10		
53	0.68	115	0.44	170	0.52		
54	0.38	116	0.24	171	0.21		
55	0.92	117	0.89	172	1.82		
56	0.31	118	0.71	173	0.69		
57	0.25	119	0.43	174	13.20		
63	0.13	120	0.54	175	2.09		
65	0.70	121	0.28	176	0.53		
66	0.25	122	0.27	184	0.08		
67	0.45	123	0.51	186	0.31		
68	0.24	128	0.21	187	0.18		
69	0.17	129	0.25	188	1.07		
70	0.13	130	0.73	189	2.05		
71.5	0.16	131	0.50	190	5.15		
72.5	0.24	132	0.86	191	11.60		
73	0.09	133	0.44	192	1.74		
77	1.20	134	0.71	193	0.17		
78	0.42	135	0.34	200	0.16		
79	0.87	136	0.17	202	0.20		
80	0.42	137	0.11	203	0.08		
81	0.23	142	0.20	204	0.32		
82	0.15	143	0.26	205	0.19		
83	0.08	144	1.08	214	0.16		
85.5	0.11	145	0.46	216	0.70		

Acrifolinol $C_{16}H_{25}O_2N$

M.w. 263

Temperature: 200°C

Electron Energy: 70 ev



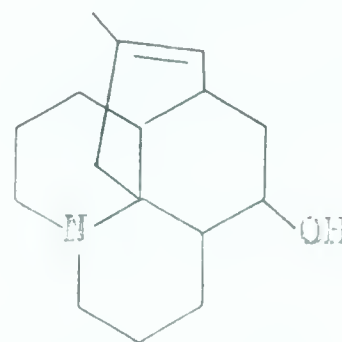
m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
27	0.68	93	0.24	147	0.58	201	0.30
28	6.24	94	0.17	148	0.46	202	0.85
29	0.79	95	0.13	149	0.44	203	0.23
30	0.38	96	0.11	150	0.18	204	1.31
31	0.14	97	0.12	154	0.19	205	0.54
38	0.13	98	0.13	155	0.10	206	0.28
39	1.05	99	0.13	156	0.28	212	0.15
40	0.34	100	0.09	157	0.21	214	0.13
41	1.93	101	0.11	158	0.71	216	0.55
42	1.03	103	0.27	159	0.33	217	0.28
43	0.85	104	0.23	160	1.30	218	0.62
44	3.89	105	0.27	161	0.50	219	0.49
45	0.28	106	0.29	162	0.55	220	0.48
51	0.25	107	0.16	163	0.21	221	0.26
52	0.12	115	0.48	164	0.11	226	0.37
53	0.49	116	0.28	167	0.13	227	0.19
54	0.32	117	0.73	168	0.19	228	0.54
55	0.84	118	0.53	169	0.11	229	0.13
56	0.30	119	0.30	170	0.89	230	0.82
57	0.66	120	0.41	171	0.33	231	0.21
58	0.11	121	0.20	172	2.24	232	0.32
63	0.12	122	0.22	173	0.80	233	0.49
65	0.46	123	0.37	174	4.45	234	0.14
66	0.17	127	0.12	175	1.34	242	0.21
67	0.38	128	0.28	176	0.50	243	0.23
68	0.21	129	0.29	177	0.18	244	1.19
69	0.38	130	0.71	178	0.13	245	1.97
70	0.69	131	0.45	184	0.31	246	1.66
71	0.20	132	0.61	185	0.15	247	0.34
77	0.83	133	0.36	186	0.77	248	0.29
78	0.30	134	0.55	187	0.27	259	0.10
79	0.59	135	0.21	188	1.19	260	0.40
80	0.33	136	0.20	189	0.62	261	0.89
81	0.24	141	0.13	190	2.63	262	0.99
82	0.13	142	0.29	191	2.46	263	1.53
83	0.23	143	0.33	192	2.93	264	0.29
89	0.11	144	1.02	193	0.50		
91	1.03	145	0.40	198	0.16		
92	0.21	146	1.38	200	0.37		

$\Delta^{8,15}$ -dehydrodihydrolycopodine $C_{16}H_{25}ON$

M.w. 247

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
26	0.08	91	1.27	138	0.30	192	0.78
27	0.73	92	0.13	141	0.08	193	0.12
28	0.95	93	0.47	142	0.10	200	0.30
29	0.80	94	0.33	143	0.18	201	0.14
30	0.46	95	0.31	144	0.39	202	0.44
31	0.65	96	0.25	145	0.27	203	0.54
39	0.91	97	0.23	146	3.08	204	0.45
40	0.19	98	0.07	147	0.58	205	0.17
41	2.26	99	0.06	148	1.03	206	0.08
42	0.92	103	0.20	149	0.41	208	0.09
43	1.93	104	0.14	150	0.22	214	0.50
44	0.82	105	0.63	151	0.06	215	0.10
45	0.08	106	0.37	152	0.08	216	0.10
51	0.25	107	0.25	156	0.10	218	0.10
52	0.16	108	0.38	157	0.11	219	0.08
53	0.76	109	0.21	158	0.34	226	0.12
54	0.62	110	0.20	159	0.20	227	0.06
55	1.30	111	0.12	160	1.51	228	0.38
56	0.49	115	0.28	161	1.14	229	0.63
57	0.47	116	0.14	162	1.74	230	0.66
58	0.13	117	0.49	163	3.44	231	0.13
63	0.08	118	0.40	164	0.58	232	0.66
65	0.55	119	0.34	165	0.12	233	0.12
66	0.22	120	0.66	170	0.25	242	0.08
67	0.71	121	0.38	171	0.11	243	0.12
68	0.35	122	0.75	172	0.86	244	1.21
69	0.34	123	0.27	173	0.50	245	1.26
70	0.32	124	0.07	174	14.90	246	1.03
71	0.24	127	0.08	175	2.22	247	4.47
77	0.98	128	0.17	176	2.05	248	0.79
78	0.31	129	0.19	177	0.34	249	0.08
79	0.94	130	0.34	178	0.14		
80	0.47	131	0.38	184	0.12		
81	0.49	132	0.56	186	0.51		
82	0.31	133	0.38	187	0.19		
83	0.23	134	1.15	188	1.23		
84	0.19	135	0.97	189	0.42		
85	0.16	136	0.16	190	3.58		
89	0.06	137	2.38	191	1.04		

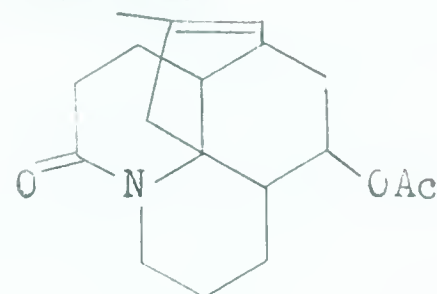
9-Oxo- $\Delta^{8,15}$ -dehydrodihydrolycconodine acetate

$C_{18}H_{25}O_3N$

M.w. 303

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
26	0.09	93	0.63	144	0.49	199	0.07
27	0.85	94	0.35	145	0.33	200	1.99
28	1.15	95	0.49	146	0.89	201	0.64
29	0.71	96	0.27	147	0.33	202	1.38
30	0.46	97	0.12	148	0.48	203	0.33
31	0.07	98	0.09	149	0.36	204	1.30
39	0.89	99	0.11	150	0.77	205	0.30
40	0.20	102	0.07	151	2.18	206	0.13
41	1.86	103	0.26	152	0.63	213	0.06
42	0.61	104	0.23	153	0.10	214	0.39
43	4.28	105	0.75	154	0.09	215	0.43
44	2.54	106	0.51	155	0.09	216	0.34
45	0.85	107	0.29	156	0.16	217	0.49
51	0.30	108	0.52	157	0.18	218	0.20
52	0.20	109	0.21	158	0.54	220	0.06
53	0.75	110	0.31	159	0.35	222	0.13
54	0.39	111	0.12	160	1.26	224	0.06
55	2.36	112	0.07	161	0.50	225	0.10
56	0.40	115	0.44	162	0.54	227	0.06
57	0.26	116	0.22	163	0.24	228	3.71
60	0.50	117	0.63	164	0.25	229	0.58
63	0.12	118	0.51	165	0.07	230	0.14
65	0.06	119	0.43	168	0.06	232	0.09
66	0.22	120	0.72	169	0.06	240	0.08
67	0.06	121	0.30	170	0.19	241	0.12
68	0.23	122	0.43	171	0.13	242	0.86
69	0.29	123	0.37	172	0.80	243	6.25
70	0.31	124	0.10	173	0.35	244	2.82
71	0.14	127	0.11	174	2.64	245	0.51
72	0.05	128	0.31	175	0.76	246	0.23
77	1.18	129	0.32	176	0.50	247	0.04
78	0.36	130	0.47	177	0.46	257	0.04
79	0.99	131	0.60	178	0.14	258	0.06
80	0.42	132	1.45	180	0.06	259	0.22
81	0.54	133	0.61	184	0.18	260	0.56
82	0.12	134	0.71	185	0.10	261	0.30
83	0.18	135	0.25	186	1.44	262	0.05
84	0.14	136	0.65	187	1.14	275	0.06
85	0.10	137	0.17	188	5.29	279	0.07
89	0.10	138	0.10	189	1.02	288	0.13
90	0.08	141	0.14	190	0.45	295	0.11
91	1.40	142	0.17	191	0.09	303	2.54
92	0.31	143	0.29	198	0.10	304	0.54
						319	0.12

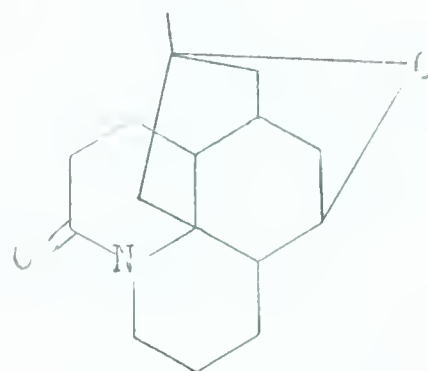
Dihydrolycopodine Lactam Ether

C₁₆H₂₃O₂N

M.W. 261

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	1.51	85	0.14	138	0.11	246	0.19
28	1.29	91	1.41	143	0.11	260	0.34
29	1.34	92	0.35	144	0.18	261	7.77
30	0.67	93	0.62	145	0.24	262	1.37
31	0.10	94	0.51	146	0.49		
32	0.11	95	0.62	147	0.34		
39	1.60	96	0.33	148	0.91		
40	0.36	97	0.11	149	0.91		
41	3.36	103	0.18	150	0.62		
42	0.89	104	0.20	151	0.61		
43	3.64	105	0.72	152	0.09		
44	0.49	106	0.62	158	0.17		
45	0.08	107	0.39	159	0.21		
51	0.33	108	0.45	160	1.11		
52	0.27	109	0.18	161	0.28		
53	1.28	110	0.18	162	1.08		
54	0.94	111	0.11	163	0.23		
55	3.04	115	0.20	164	0.20		
56	0.64	116	0.13	172	0.13		
57	0.46	117	0.47	173	0.11		
58	0.17	118	0.38	174	0.51		
63	0.11	119	0.45	175	0.44		
64	0.08	120	0.74	176	1.70		
65	0.77	121	0.50	177	4.13		
66	0.45	122	0.50	178	0.60		
67	1.12	123	0.23	186	0.19		
68	0.48	124	0.12	187	0.47		
69	0.29	125	0.08	188	12.90		
70	0.57	128	0.10	189	1.94		
71	0.19	129	0.14	190	1.85		
77	1.25	130	0.22	202	0.34		
78	0.41	131	0.42	203	0.31		
79	1.20	132	0.92	204	6.27		
80	0.62	133	0.45	205	2.08		
81	0.63	134	0.99	206	0.67		
82	0.42	135	0.41	218	0.33		
83	0.22	136	0.55	232	0.11		
84	0.13	137	0.20	233	0.05		

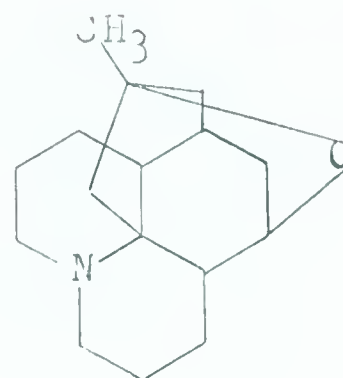
Dihydrolyconopodine 5,15 Ether

$C_{16}H_{25}ON$

M.w. 247

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	0.70	94	0.43	150	0.63		
28	0.96	95	0.47	158	0.27		
29	1.10	96	0.33	159	0.20		
30	0.56	97	0.27	160	0.96		
39	0.73	103	0.17	161	0.66		
40	0.20	104	0.17	162	2.06		
41	2.69	105	0.70	163	5.55		
42	1.16	106	0.47	164	0.86		
43	3.26	107	0.33	165	0.13		
44	1.26	108	0.50	170	0.23		
45	0.30	109	0.27	172	0.63		
51	0.17	110	0.30	173	0.43		
52	0.13	111	0.13	174	16.50		
53	0.90	115	0.20	175	2.39		
54	0.86	116	0.13	176	2.89		
55	1.93	117	0.50	177	0.43		
56	0.66	118	0.43	178	0.20		
57	0.50	119	0.40	186	0.20		
58	0.23	120	0.76	188	0.80		
59	0.13	121	0.47	189	0.30		
65	0.43	122	0.66	190	4.19		
66	0.23	123	0.30	191	1.33		
67	0.93	130	0.30	192	0.40		
68	0.47	131	0.37	202	0.20		
69	0.42	132	0.56	204	0.23		
70	0.40	133	0.40	230	0.17		
71	0.23	134	0.12	232	0.20		
77	0.93	135	0.12	244	1.26		
78	0.30	136	1.00	245	1.03		
79	1.06	137	1.23	246	0.80		
80	0.60	138	0.17	247	4.32		
81	0.70	143	0.13	248	0.76		
82	0.43	144	0.30				
83	0.33	145	0.23				
84	0.20	146	3.02				
91	1.23	147	0.56				
92	0.30	148	1.06				
93	0.60	149	0.33				

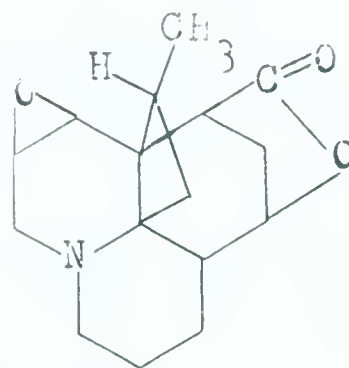
Annotinine

$C_{16}H_{21}O_3N$

M.w. 275

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
28	1.51	84.5	0.27	156	1.20		
29	0.85	89	0.30	157	0.36		
30	0.28	90	0.16	158	1.84		
31	0.21	91	1.10	159	0.62		
37	0.36	92	0.27	160	2.20		
38	0.59	93	0.26	161	0.93		
39	3.70	94	0.18	162	0.25		
40	0.78	102	0.19	166	0.19		
41	4.43	103	0.31	167	0.75		
42	2.20	104	0.26	168	1.00		
43	0.57	105	0.38	169	0.60		
44	4.37	106	0.25	170	8.75		
45	0.22	115	0.70	171	2.69		
50	0.23	116	0.34	172	1.03		
51	0.84	117	0.72	173	0.28		
52	0.47	118	0.47	174	0.30		
53	0.96	119	0.25	176	0.34		
54	0.47	120	0.50	177	0.26		
55	0.88	127	0.16	186	0.82		
56	0.22	128	0.36	187	0.39		
57	0.14	129	0.32	188	1.47		
63	0.50	130	1.18	189	2.46		
64	0.19	131	0.44	190	0.53		
65	0.12	132	0.83	204	2.32		
66	0.28	133	0.60	205	0.38		
67	0.43	134	0.34	213	0.47		
68	0.22	139	0.13	214	5.35		
69	0.13	140	0.14	215	4.00		
70	0.21	141	0.35	216	1.32		
71.5	0.41	142	1.49	217	0.36		
75	0.16	143	0.66	218	0.21		
76	0.16	144	0.50	232	0.76		
77	1.45	145	0.19	233	1.49		
77.5	0.34	146	0.49	234	0.21		
78	0.61	147	0.17	257	0.19		
79	0.63	148	0.50				
80	0.34	149	0.30				
81	0.19	154	0.93				
83.5	0.50	155	0.31				

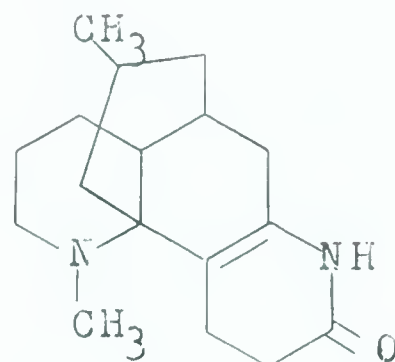
α -Obscurine

$C_{17}H_{26}ON_2$

M.w. 274

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ 25	m/e	% Σ 25	m/e	% Σ 25	m/e	% Σ 25
27	0.94	94	0.68	160	0.55		
28	1.26	95	0.27	161	0.57		
29	1.16	96	0.22	162	0.92		
30	0.60	103	0.18	163	0.65		
31	0.74	104	0.20	164	1.13		
32	0.51	105	0.36	165	0.28		
39	1.03	106	0.50	172	0.33		
40	0.23	107	0.36	173	0.28		
41	2.14	108	0.33	174	0.48		
42	2.66	109	0.15	175	0.51		
43	0.76	110	0.20	176	0.24		
44	3.98	111	0.69	186	0.14		
45	0.14	115	0.27	187	0.24		
51	0.24	116	0.18	188	0.32		
52	0.24	117	0.38	189	5.00		
53	0.74	118	0.40	190	0.89		
54	0.50	119	0.29	201	0.23		
55	2.14	120	0.93	202	0.28		
56	0.37	121	0.23	203	1.12		
57	0.14	122	0.36	204	0.40		
65	0.61	128	0.15	215	0.43		
66	0.37	129	0.14	216	0.36		
67	0.65	130	0.40	217	25.20		
68	0.70	131	0.36	218	4.07		
69	0.18	132	0.64	219	0.48		
70	1.02	133	0.36	230	0.10		
73	0.19	134	0.82	231	3.95		
77	0.92	135	0.32	232	0.32		
78	0.32	136	0.27	245	0.06		
79	0.73	137	0.13	259	0.23		
80	0.87	143	0.13	273	0.23		
81	0.56	144	0.31	274	3.47		
82	0.52	145	0.29	275	0.64		
83	0.20	146	0.73				
84	1.31	147	0.45				
87	0.43	148	1.03				
91	0.90	149	0.28				
92	0.25	158	0.20				
93	0.42	159	0.28				

Sauroxine

$C_{17}H_{26}ON_2$

M.w. 274

Temperature: 200°C

Electron Energy: 70 ev

m/e	%	25	m/e	%	25	m/e	%	25	m/e	%	25
25	0.08		76	0.10		128	0.20		187	0.24	
26	0.40		77	0.93		129	0.16		188	0.27	
27	1.04		78	0.31		130	0.46		189	4.89	
28	1.19		79	0.59		131	0.48		190	1.01	
29	0.89		80	0.82		132	0.68		191	0.27	
30	0.40		81	0.42		133	0.37		200	0.11	
31	0.38		82	0.86		134	0.64		201	0.27	
32	0.26		83	0.39		135	0.28		202	0.22	
36	0.08		84	0.44		136	0.20		203	1.87	
37	0.17		87	0.41		137	0.10		204	0.47	
38	0.26		88	0.12		142	0.13		215	0.41	
39	1.08		89	0.13		143	0.21		216	0.23	
40	0.27		90	0.09		144	0.48		217	14.3	
41	1.45		91	0.86		145	0.49		218	3.68	
42	2.20		92	0.27		146	0.87		219	0.45	
43	7.29		93	0.37		147	0.51		229	0.18	
44	3.02		94	0.56		148	1.33		230	0.10	
45	0.15		95	0.25		149	0.40		231	5.02	
50	0.13		96	0.26		150	0.16		232	0.88	
51	0.34		97	0.12		156	0.09		233	0.10	
52	0.23		103	0.27		157	0.11		245	0.09	
53	0.51		104	0.23		158	0.28		257	0.10	
54	0.45		105	0.55		159	0.32		259	0.50	
55	1.29		106	0.47		160	1.19		272	0.16	
56	0.33		107	0.26		161	1.22		273	0.30	
57	0.41		108	0.24		162	0.63		274	2.83	
58	1.75		109	0.14		163	0.63		275	0.55	
59	0.09		110	0.17		164	0.48				
63	0.16		111	0.90		165	0.09				
64	0.13		112	0.09		170	0.08				
65	0.55		115	0.33		171	0.09				
66	0.34		116	0.21		172	0.18				
67	0.50		117	0.48		173	0.25				
68	0.59		118	0.47		174	0.45				
69	0.16		119	0.33		175	0.58				
70	0.43		120	1.33		176	0.25				
72	0.09		121	0.29		177	0.19				
73	0.23		122	0.34		178	0.37				
74	0.16		123	0.12		186	0.12				

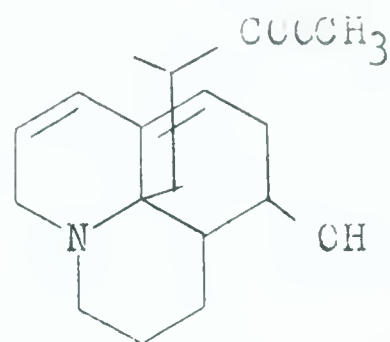
Lyconnotine

$C_{17}H_{25}O_3N$

M.W. 291

Temperature: 200°C

Electron Energy: 70 ev



m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
26	0.12						
27	1.07	80	0.20	147	0.12	211	0.25
28	3.07	81	0.10	152	0.12	212	0.17
29	3.00	87	0.22	153	0.12	216	0.75
30	0.50	88	0.12	154	0.95	217	0.12
31	3.50	89	0.37	155	0.27	224	0.17
32	2.24	90	0.15	156	0.47	257	0.10
38	0.15	91	0.85	157	0.25	258	1.40
39	1.35	92	0.17	158	0.70	259	1.00
40	0.35	93	0.12	159	0.25	260	0.30
41	2.44	100	0.10	160	0.80	270	0.07
42	0.92	101	0.12	161	0.20	290	0.07
43	1.15	102	0.25	166	0.22	291	0.05
44	1.20	103	0.40	167	0.80		
45	0.95	104	0.25	168	1.07		
50	1.00	105	0.27	169	0.42		
51	0.35	106	0.17	170	8.04		
52	0.20	114	0.12	171	2.34		
53	0.40	115	0.95	172	9.48		
54	0.22	116	0.55	173	1.90		
55	0.72	117	1.02	174	0.55		
56	0.30	118	0.62	180	0.25		
57	0.32	119	0.22	181	0.12		
58	0.22	120	0.15	182	0.25		
59	0.82	127	0.20	183	0.30		
63	0.25	128	0.35	184	0.22		
65	0.50	129	0.37	186	0.15		
66	0.12	130	0.13	188	1.75		
67	0.20	131	0.47	189	0.37		
68	0.15	132	0.50	190	6.99		
69	0.37	133	0.17	191	0.12		
70	0.15	139	0.15	192	0.32		
71	0.15	140	0.15	194	0.27		
73	0.17	141	0.32	196	0.57		
75	0.12	142	1.87	203	0.10		
76	0.10	143	0.97	205	0.12		
77	1.05	144	3.42	208	0.20		
78	0.40	145	0.57	209	0.12		
79	0.42	146	0.50	210	0.55		

Diol from L. Clavatum

$C_{16}H_{25}O_2N$

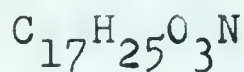
M.W. 263

Temperature: 200°C

Electron Energy: 70 ev

m/e	% Σ 25	m/e	% Σ 25	m/e	% Σ 25	m/e	% Σ 25
27	0.74	89	0.09	135	0.44	179	0.11
28	3.52	91	1.11	136	0.35	184	0.18
29	1.30	92	0.26	137	0.25	185	0.09
30	0.37	93	0.48	141	0.11	186	0.40
31	0.27	94	0.33	142	0.14	187	0.17
32	0.46	95	0.58	143	0.23	188	3.48
39	0.86	96	0.25	144	0.51	189	0.67
40	0.22	97	0.52	145	0.33	190	1.20
41	2.43	98	0.11	146	1.10	200	0.62
42	1.03	99	0.11	147	0.77	201	0.55
43	1.35	103	0.25	148	0.76	202	5.66
44	0.67	104	0.24	149	0.33	203	14.10
45	0.09	105	0.64	150	0.35	204	2.82
51	0.26	106	0.44	151	0.19	205	0.42
52	0.17	107	0.39	152	0.10	206	0.59
53	0.65	108	0.26	153	0.11	207	0.19
54	0.36	109	0.41	154	0.11	208	0.59
55	1.74	110	0.16	155	0.10	209	0.13
56	0.50	111	0.33	156	0.18	216	0.37
57	1.28	115	0.36	157	0.18	217	0.13
58	0.11	116	0.18	158	0.59	218	0.33
63	0.10	117	0.63	159	0.40	219	0.09
65	0.53	118	0.49	160	2.88	220	0.65
66	0.20	119	0.45	161	1.60	221	0.20
67	0.81	120	0.56	162	1.04	226	0.11
68	0.34	121	0.33	163	0.28	228	0.27
69	0.91	122	0.38	164	0.21	230	0.11
70	0.35	123	0.69	165	0.15	232	0.23
71	0.52	124	0.12	167	0.09	233	0.15
77	0.97	125	0.18	168	0.09	234	0.22
78	0.33	127	0.11	169	0.09	242	0.11
79	0.86	128	0.20	170	0.26	244	0.28
80	0.44	129	0.21	171	0.14	245	0.18
81	0.75	130	0.51	172	0.58	246	1.05
82	0.32	131	0.45	173	0.33	247	0.79
83	0.62	132	0.77	174	1.05	248	0.21
84	0.18	133	0.55	175	0.55	262	1.11
85	0.33	134	0.70	176	0.52	263	2.13
				177	0.18	264	0.40
				178	0.28		

Annopodine



M.w. 291

Temperature: 200°C

Electron Energy: 70 ev

m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
27	0.94	90	0.12	148	0.25	206	0.16
28	1.81	91	1.02	149	0.12	212	0.22
29	1.19	92	0.25	150	0.12	214	0.66
30	0.45	93	0.30	152	0.12	215	0.22
31	0.25	94	0.27	154	0.18	216	2.71
32	0.19	95	0.13	155	0.16	217	0.52
39	1.03	96	0.15	156	0.36	218	0.60
40	0.23	103	0.31	157	0.25	219	0.45
41	2.26	104	0.27	158	0.81	220	0.52
42	0.90	105	0.46	159	0.32	228	0.18
43	0.73	106	0.35	160	1.06	230	0.56
44	0.69	107	0.24	161	0.32	231	0.23
45	0.19	108	0.22	162	0.40	232	1.63
51	0.42	115	0.54	163	0.12	233	1.42
52	0.28	116	0.28	164	0.11	234	3.84
53	0.82	117	0.69	165	0.11	235	0.56
54	0.51	118	0.56	168	0.18	236	0.17
55	1.13	119	0.29	169	0.17	246	1.20
56	0.37	120	0.40	170	1.08	247	0.42
57	0.32	121	0.16	171	0.39	248	16.9
59	0.43	122	0.16	172	0.91	249	4.69
63	0.18	127	0.13	173	0.26	250	0.65
64	0.11	128	0.33	174	0.42	258	0.16
65	0.64	129	0.32	176	0.21	260	0.91
66	0.24	130	0.71	184	0.24	261	0.24
67	0.48	131	0.44	185	0.12	262	0.15
68	0.35	132	0.65	186	0.52	274	0.94
69	0.28	133	0.33	187	0.52	275	0.19
70	0.24	134	0.60	188	2.12	276	1.59
77	1.08	135	0.17	189	0.70	277	0.30
78	0.44	136	0.14	190	2.11	278	0.08
79	0.65	141	0.19	191	0.59	289	0.29
80	0.41	142	0.36	192	0.15	290	0.52
81	0.27	143	0.41	198	0.24	291	1.89
82	0.28	144	0.83	200	0.22	292	0.36
83	0.13	145	0.35	202	0.31		
84	0.13	146	0.68	204	0.37		
89	0.14	147	0.27	205	0.17		

Cernuine

$C_{16}H_{26}ON_2$

M.w. 262

Temperature: 200°C

Electron Energy: 70 ev

m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
26	0.15	85	0.05	147	0.13	218	0.10
27	1.04	91	0.21	148	0.37	219	4.11
28	2.76	92	0.09	149	0.50	220	6.42
29	0.97	93	0.38	150	1.46	221	1.06
30	0.84	94	0.73	151	1.61	222	0.10
38	0.06	95	0.70	152	0.34	231	0.12
39	0.81	96	1.05	153	0.20	232	0.07
40	0.30	97	0.50	154	0.05	233	8.58
41	4.42	98	1.07	160	0.08	234	2.05
42	1.55	99	0.13	161	0.14	235	0.23
43	0.97	105	0.11	162	0.20	243	0.11
44	2.90	106	0.20	163	1.11	245	0.17
45	0.37	107	0.40	164	1.69	247	1.21
51	0.08	108	0.74	165	1.20	248	0.28
52	0.09	109	0.76	166	0.48	256	0.10
53	0.73	110	0.95	167	0.11	259	0.17
54	2.04	111	0.37	168	0.05	260	0.18
55	3.99	112	0.30	174	0.05	261	1.30
56	0.89	117	0.05	175	0.12	262	4.06
57	0.26	118	0.07	176	0.13	263	0.71
58	0.08	119	0.10	177	0.56	264	0.06
61	0.05	120	0.25	178	1.30		
65	0.17	121	0.48	179	0.36		
66	0.15	122	0.80	180	0.08		
67	1.05	123	0.99	185	0.05		
68	0.98	124	0.48	188	0.05		
69	1.14	125	0.10	189	0.24		
70	0.86	126	0.07	190	0.19		
71	0.14	131	0.07	191	1.83		
75	0.19	132	0.09	192	1.01		
77	0.22	133	0.10	193	0.41		
78	0.08	134	0.35	194	0.06		
79	0.45	135	0.23	203	0.11		
80	0.72	136	1.14	204	0.10		
81	1.05	137	0.47	205	1.45		
82	1.54	138	0.31	206	0.83		
83	0.50	139	0.06	207	0.22		
84	0.31	146	0.08	217	0.18		

Dihydrodeoxycernuine

$C_{16}H_{28}N_2$

M.w. 248

Temperature: 200°C

Electron Energy: 70 ev

m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.12	93	0.40	153	0.13	249	0.48
27	0.92	94	0.80	161	0.11		
28	2.52	95	0.70	162	0.17		
29	0.83	96	0.24	163	0.71		
30	0.61	97	1.08	164	1.82		
32	0.14	98	0.34	165	0.57		
39	1.00	103	0.39	166	0.16		
40	0.30	105	0.11	175	0.14		
41	3.24	106	0.24	176	0.20		
42	1.41	107	0.29	177	1.98		
43	0.69	108	0.92	178	0.75		
44	0.28	109	0.55	179	0.34		
51	0.15	110	1.17	189	0.22		
52	0.14	111	0.54	190	0.18		
53	0.76	112	0.11	191	1.90		
54	1.59	116	0.10	192	0.61		
55	2.29	117	0.13	193	0.19		
56	1.17	118	0.11	203	0.31		
57	0.18	119	0.12	204	0.30		
58	0.12	120	0.26	205	5.28		
65	0.26	121	0.27	206	6.32		
66	0.19	122	0.84	207	0.92		
67	1.11	123	0.79	208	0.16		
68	1.17	124	0.51	217	0.21		
69	1.10	125	0.10	218	0.15		
70	0.38	132	0.10	219	7.30		
77	0.31	133	0.10	220	1.66		
78	0.13	134	0.44	221	0.29		
79	0.53	135	0.55	231	0.33		
80	0.86	136	3.06	232	0.30		
81	0.86	137	1.62	233	1.55		
82	1.57	138	1.29	234	0.45		
83	0.58	139	0.20	235	0.13		
84	2.61	148	0.31	236	0.19		
85	0.19	149	0.52	245	0.70		
89	0.10	150	3.60	246	0.46		
91	0.26	151	2.43	247	2.41		
92	0.11	152	0.66	248	3.33		

Lycocernuine



M.w. 278

Temperature: 200°C

Electron Energy: 70 ev

m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
27	1.57	95	0.70	166	2.04		
28	3.34	96	1.48	167	0.47		
29	1.32	97	1.87	168	0.14		
30	0.71	98	1.41	177	0.21		
31	0.18	99	0.18	178	0.49		
39	1.21	106	0.26	179	0.22		
40	0.40	107	0.33	180	0.37		
41	4.46	108	0.54	181	0.11		
42	1.64	109	0.49	191	0.54		
43	1.16	110	1.44	192	0.38		
44	1.02	111	0.50	193	0.51		
45	0.21	112	0.45	194	0.39		
51	0.14	120	0.34	205	0.83		
52	0.14	121	0.38	206	0.24		
53	0.91	122	0.61	207	0.39		
54	2.20	123	0.52	217	0.14		
55	4.46	124	0.68	218	0.15		
56	1.07	125	0.26	219	9.18		
57	0.58	126	0.17	220	5.57		
58	0.13	132	0.13	221	1.62		
65	0.26	134	0.26	222	0.27		
66	0.21	135	0.18	233	1.03		
67	1.16	136	0.44	234	0.22		
68	1.45	137	0.33	235	0.49		
69	1.95	138	0.75	236	0.13		
70	1.21	139	0.17	247	0.31		
71	0.26	146	0.14	248	0.11		
77	0.35	147	0.12	249	2.14		
78	0.14	148	0.29	250	0.82		
79	0.52	149	0.41	259	0.14		
80	0.96	150	0.49	261	1.47		
81	0.98	151	0.64	262	0.48		
82	1.81	152	2.76	263	0.24		
83	0.52	153	0.43	276	0.18		
84	0.27	162	0.36	277	0.47		
91	0.22	163	0.46	278	1.85		
93	0.53	164	0.61	279	0.32		
94	0.92	165	3.22				

Dihydrodeoxyglycocernuine

$C_{16}H_{28}ON_2$

M.W. 264

Temperature: 200°C

Electron Energy: 70 ev

m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}	m/e	% \sum_{25}
26	0.15	91	0.25	139	0.32	204	0.19
27	1.13	92	0.13	140	0.12	205	9.15
28	3.22	93	0.45	144	0.12	206	3.33
29	1.17	94	0.86	146	0.19	207	0.62
30	0.87	95	0.63	147	0.14	208	0.17
31	0.16	96	1.20	148	0.53	217	0.09
32	0.10	97	1.89	149	0.47	218	0.13
38	0.09	98	0.67	150	1.14	219	0.88
39	1.05	99	0.15	151	2.22	220	0.27
40	0.32	100	0.10	152	2.22	221	0.53
41	3.94	103	0.08	153	0.28	222	0.10
42	1.76	105	0.12	154	0.30	231	0.28
43	1.19	106	0.31	160	0.10	232	0.11
44	1.21	107	0.26	161	0.08	233	0.20
45	0.09	108	0.59	162	0.27	234	0.14
51	0.14	109	0.29	163	0.27	235	1.55
52	0.14	110	1.56	164	0.77	236	0.89
53	0.77	111	1.04	165	0.22	237	0.14
54	1.67	112	0.34	166	1.79	243	0.09
55	2.36	113	0.12	167	0.90	244	0.11
56	1.50	117	0.12	168	0.92	245	0.39
57	0.49	118	0.13	169	0.13	246	0.19
58	0.22	119	0.12	172	0.11	247	1.49
65	0.25	120	0.32	174	0.18	248	0.41
66	0.19	121	0.22	175	0.09	249	0.31
67	1.03	122	0.86	176	0.09	261	0.11
68	1.64	123	0.70	177	0.43	263	1.74
69	1.84	124	1.83	178	0.26	264	1.03
70	0.49	125	0.48	179	0.43	265	0.18
71	0.27	126	0.22	180	0.55		
77	0.32	130	0.08	181	0.21		
78	0.13	131	0.08	182	0.11		
79	0.49	132	0.19	189	0.12		
80	0.89	133	0.10	190	0.12		
81	0.77	134	0.46	191	0.53		
82	1.44	135	0.25	192	0.29		
83	0.59	136	0.48	193	0.25		
84	2.01	137	1.04	194	0.08		
85	0.17	138	1.84	203	0.29		

Diacetyl Serratinine

$C_{20}H_{29}O_5N$

M.W. 363

Temperature: 200°C

Electron Energy: 70 ev

m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}	m/e	% Σ_{25}
26	0.08	93	0.38	144	0.12	198	0.07
27	0.43	94	0.32	145	0.11	200	0.24
28	1.09	95	0.22	146	0.64	201	0.05
29	0.53	96	0.44	147	0.31	202	0.12
30	0.36	97	0.81	148	1.88	204	0.09
39	0.43	98	0.12	149	4.36	207	0.07
40	0.12	103	0.11	150	3.74	208	0.10
41	1.54	104	0.09	151	1.01	214	0.26
42	0.92	105	0.50	152	7.20	215	0.12
43	4.63	106	0.32	153	0.76	216	3.36
44	0.67	107	0.25	154	0.07	217	0.46
45	0.48	108	0.40	156	0.06	218	0.16
51	0.12	109	0.18	158	0.18	220	0.07
52	0.09	110	0.50	159	0.10	232	0.93
53	0.39	111	0.11	160	0.43	233	0.19
54	0.23	112	0.06	161	0.15	234	0.19
55	0.64	115	0.12	162	0.45	242	0.06
56	0.45	116	0.08	163	0.12	244	0.30
57	0.40	117	0.28	164	0.16	245	0.05
58	0.07	118	0.23	165	0.11	260	0.23
60	0.30	119	0.29	166	0.05	261	0.05
63	0.05	120	0.95	170	0.10	262	0.07
65	0.30	121	0.32	171	0.06	274	0.27
66	0.15	122	1.24	172	0.32	275	0.27
67	0.45	123	0.85	173	0.11	276	19.70
68	0.30	124	0.28	174	0.33	277	3.82
69	0.27	125	0.05	175	0.12	278	0.47
70	0.30	126	0.04	176	0.81	292	0.68
71	0.13	127	0.04	177	0.23	293	0.13
77	0.52	128	0.07	178	0.20	304	0.16
78	0.16	129	0.09	184	0.08	322	0.11
79	0.51	130	0.15	186	0.25	336	1.27
80	0.39	131	0.19	187	0.08	337	0.27
81	0.30	132	0.26	188	0.24	362	0.02
82	0.19	133	0.36	189	0.12	363	0.02
83	0.20	134	0.73	190	0.12		
84	0.31	135	0.22	192	0.08		
85	0.08	136	0.74	194	5.02		
91	0.63	137	0.10	195	0.62		
92	0.18	143	0.07	196	0.08		

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